Model System Diagnostics

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2020 DOE VTO Annual Merit Review
June 1-4, 2020

Project ID: bat225

Overview

Timeline

- Start date: October 2019
- End date: September 2022
- Percent complete: 25%

Budget

- Total project funding
  - FY2020 $550K

Barriers Addressed

- Energy density
- Cycle life
- Safety

Partners

- Interactions/collaborations: LBNL, UCB, ANL, Cambridge, ORNL, PNNL, NCEM, ALS, SSRL
- Project lead: Vincent Battaglia

Relevance/Objectives

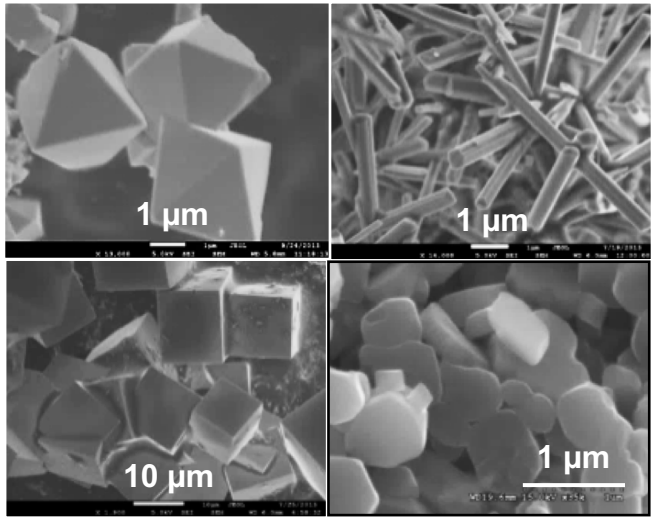
- Use model systems to obtain fundamental understanding on performance-limiting properties, phase transition mechanisms, kinetic barriers, and instabilities in materials for high-energy lithium batteries
- Develop strategies to improve solid-state charge transport and optimize charge transfer at electrode-electrolyte interface
- Discover and develop next-generation materials and interfaces based on rational design as opposed to the conventional empirical approaches

Milestones

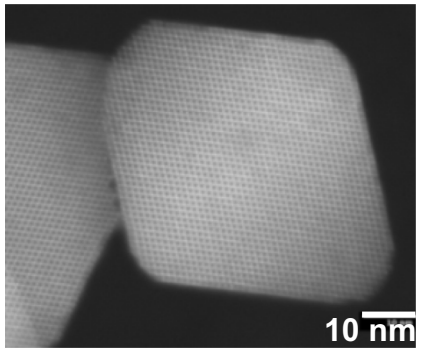
Date	Milestones	Status
December 2019	Evaluate the effect of surface treatment on anion redox-active TM oxide cathodes	Completed
March 2020	Provide insights on factors influencing performance of anion redox-active TM oxide cathodes	Completed
June 2020	Advanced diagnostic studies of solid-state electrolyte model samples at both particle-level and bulk-sample level	On Schedule
September 2020	Obtain understanding on solid-state electrolyte grain and grain boundary properties and their effect on ion conduction	On Schedule

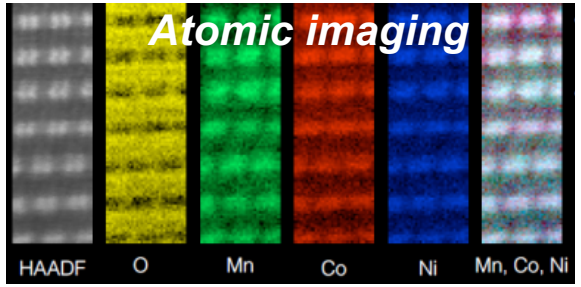
Approach/Strategy

High-quality model samples with well-controlled physical properties

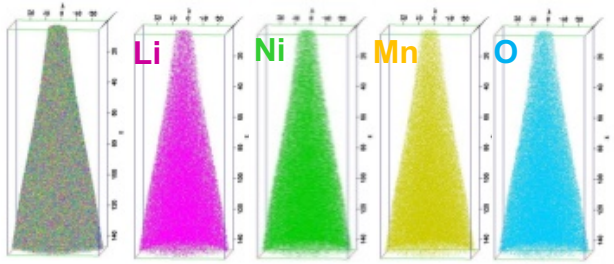


Fundamental understanding of solid-state chemistry, kinetic barriers and instabilities during battery operation





3D compositional mapping



Model-system construction

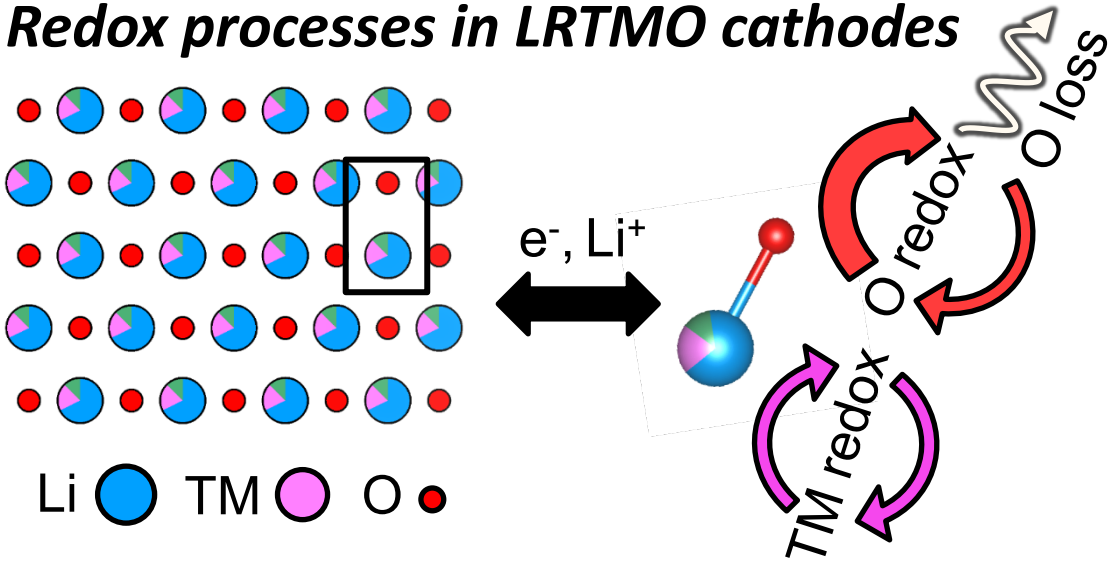
Advanced diagnostics

Rational design, synthesis and testing of materials

Fundamental knowledge

The good and bad of O redox in Li-rich TM oxide (LRTMO) cathodes

Redox processes in LRTMO cathodes



The good

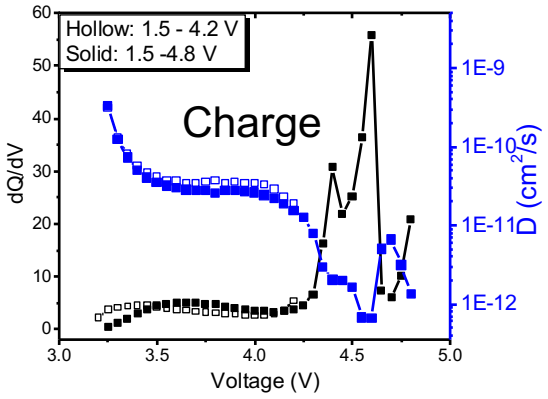
- Combined TM and O redox provides higher energy density (up to 1000 wh/kg)
- A wide chemistry space with the potential to develop low-cost cathode materials

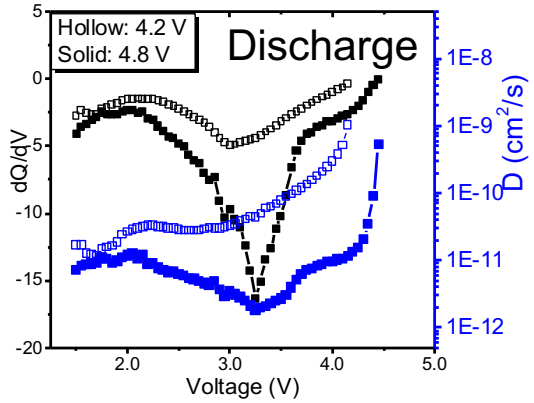
The bad

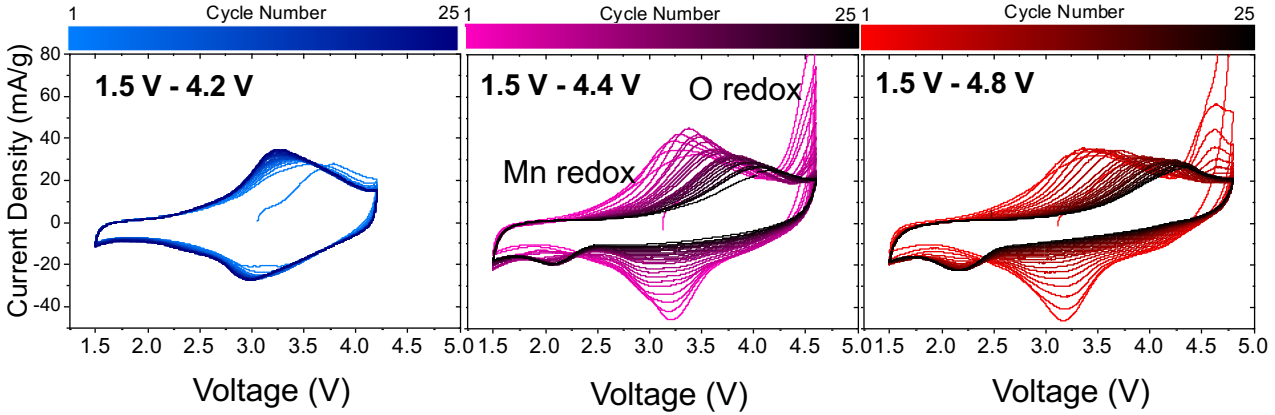
- Decreasing chemical, structural, mechanical and cycling stabilities with the increase use of O redox at high voltages

The bad

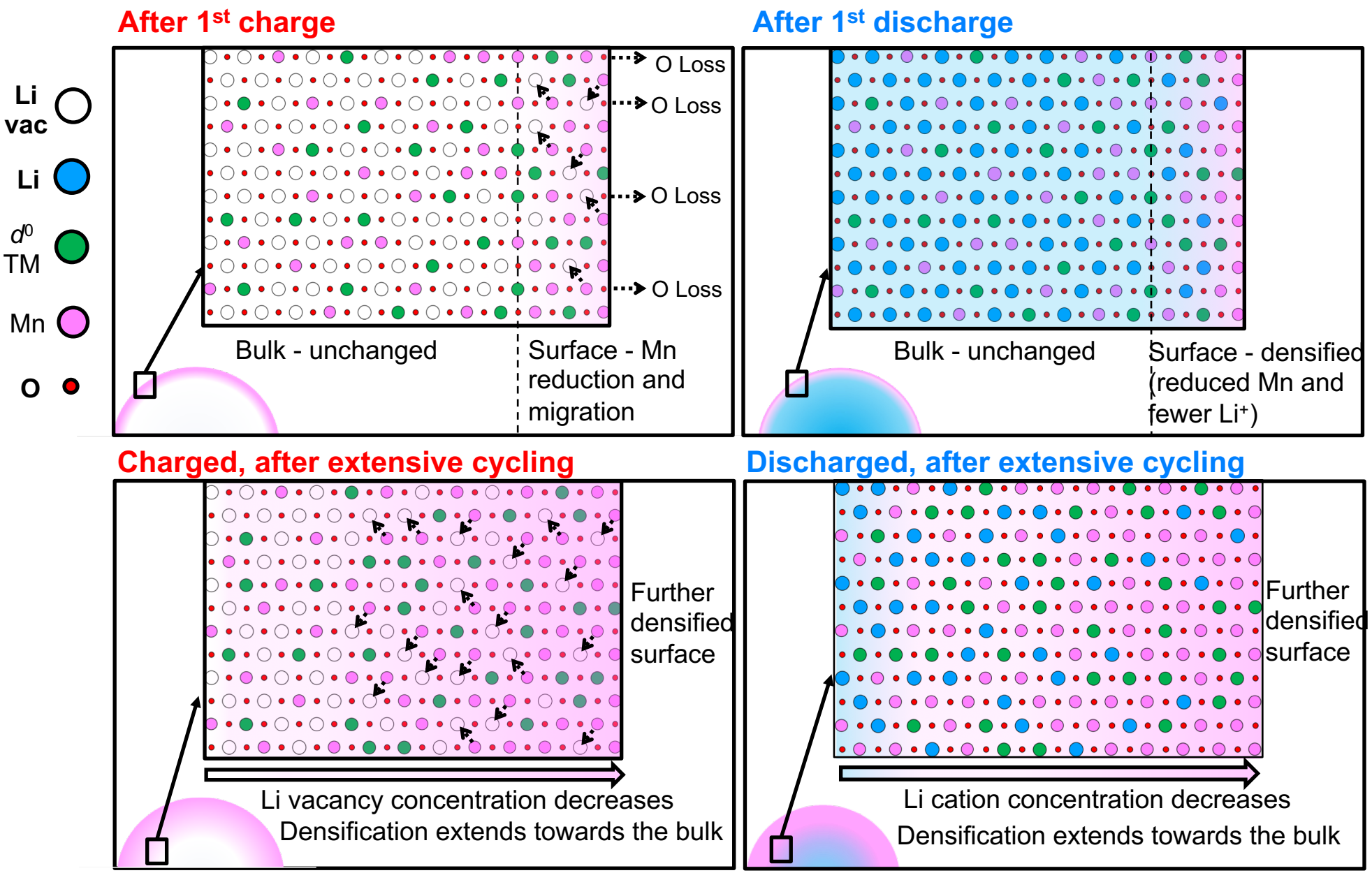
- Rate limitation – oxygen redox slower than TM redox





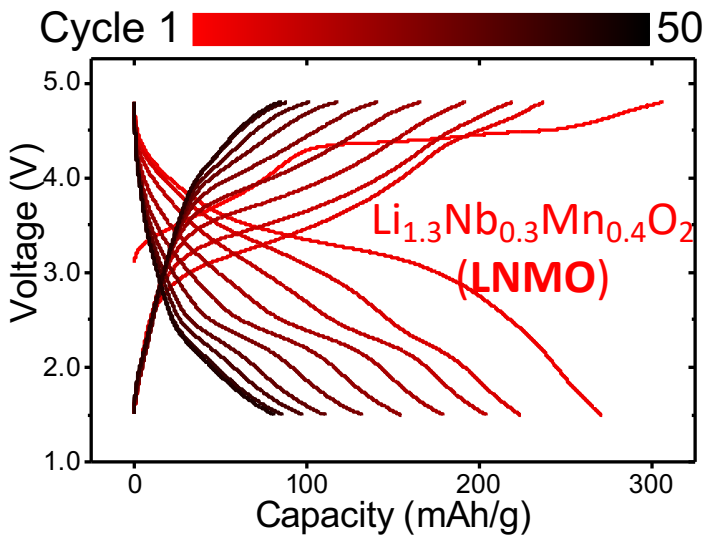


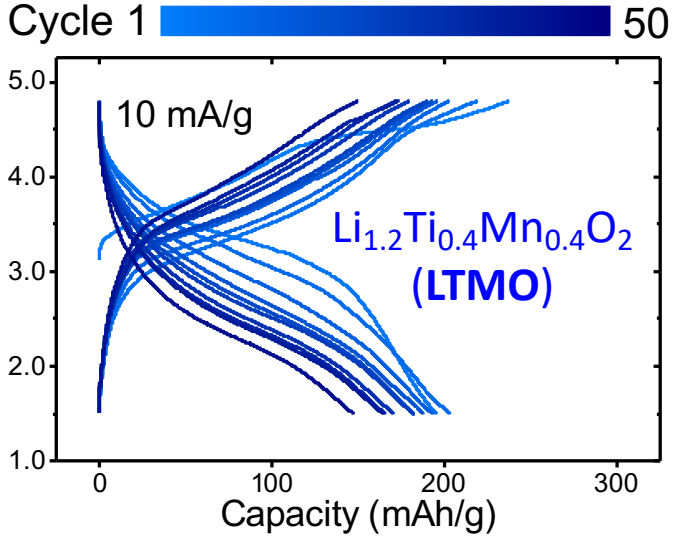
Technical Accomplishments: degradation mechanism in rocksalt LRTMO cathode revealed

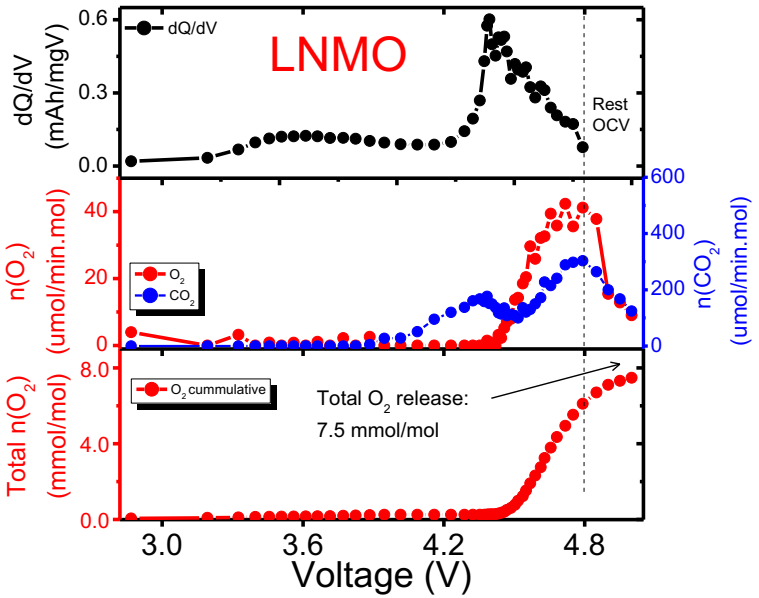


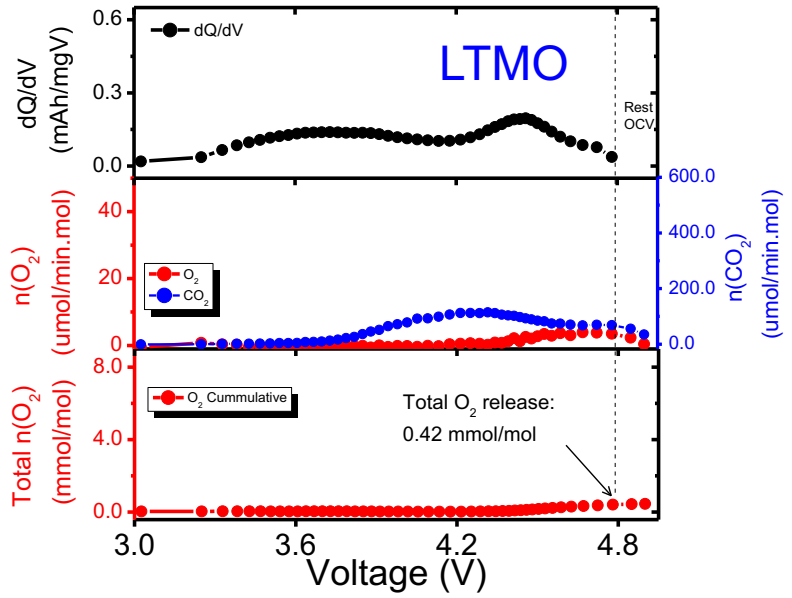
- 1st charge – loss of lattice O creates vacancies on surface. Reduced TM cations migrate into the neighboring Li^+ sites.
- 1st discharge – Li cations reinserted but reduced Li content on surface due to loss of Li sites to TM cations.
- Densification continues in the following cycles, leading to Li gradient and TM reduction towards bulk.

Mitigating Strategy I – Chemistry Engineering



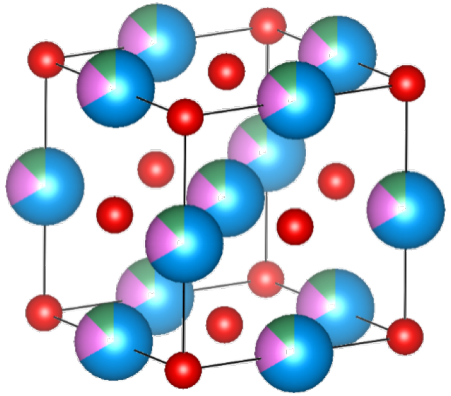


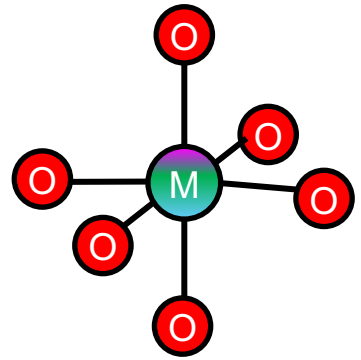




Differential Electrochemical Mass Spectroscopy *(DEMS, with B. McCloskey, UC Berkeley)*

Rocksalt LRTMO



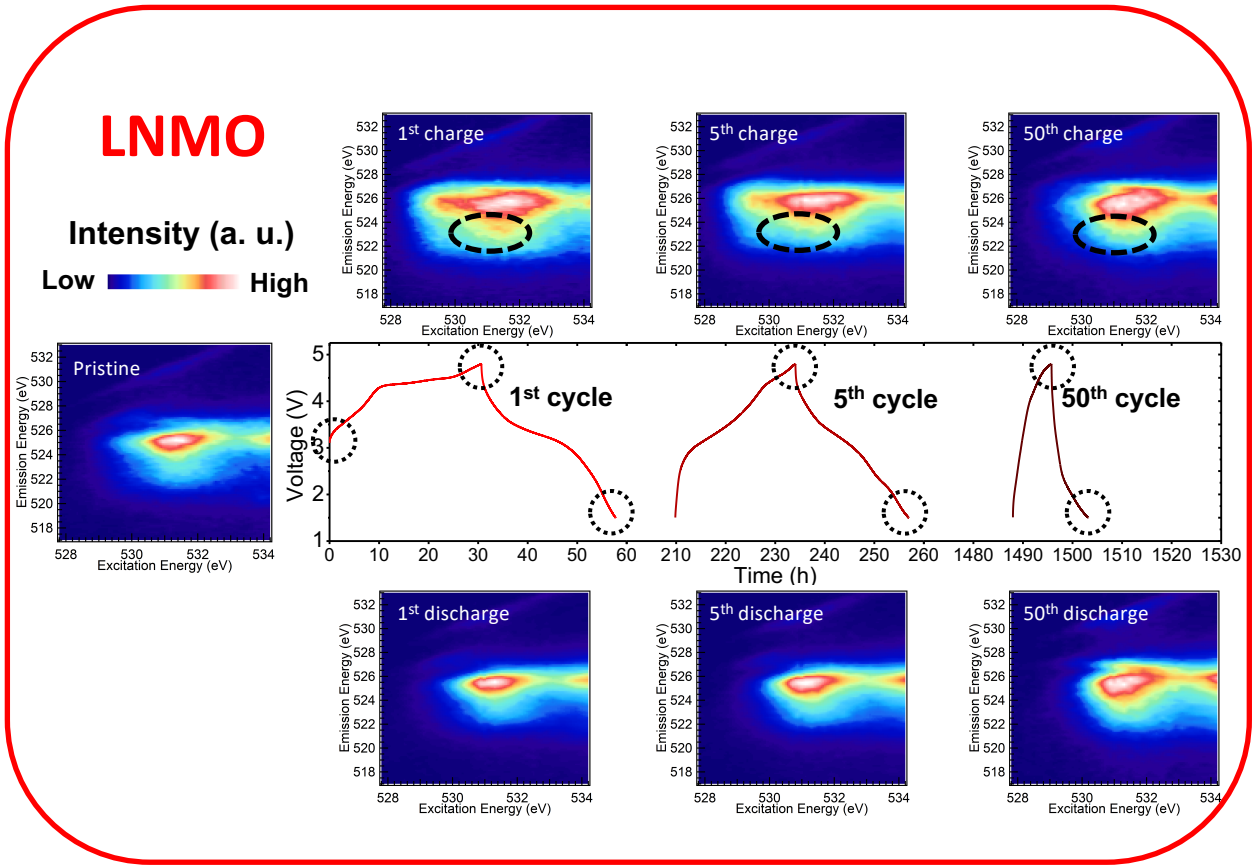


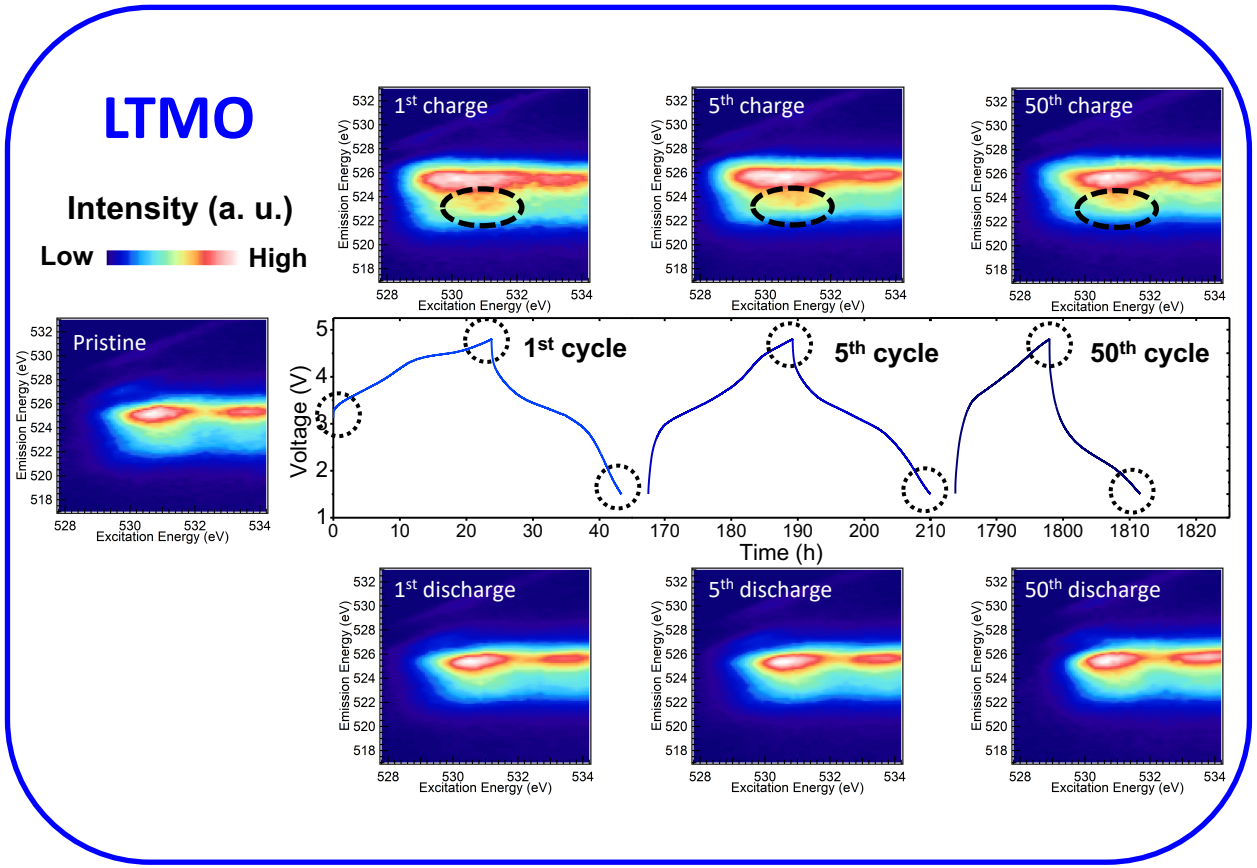
M = Li and TM (redox active and inactive)

- Samples prepared to have the same redox-active Mn content but different redox-inactive TM of Nb or Ti
- Redox-inactive TM influences electrochemical performance – LTMO more stable than LNMO
- Redox-inactive TM influences oxygen loss – about 20x less in LTMO than LNMO

Strategy I – role of redox-inactive TM

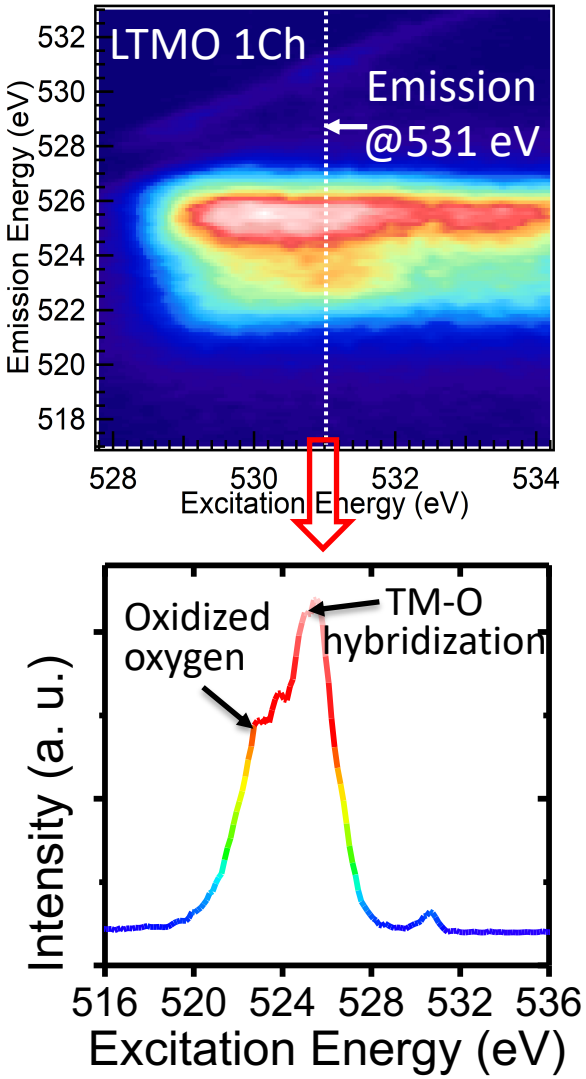
Resonant Inelastic X-ray Scattering Mapping *(RIXS, with W. Yang, ALS beamline 8.0.1)*

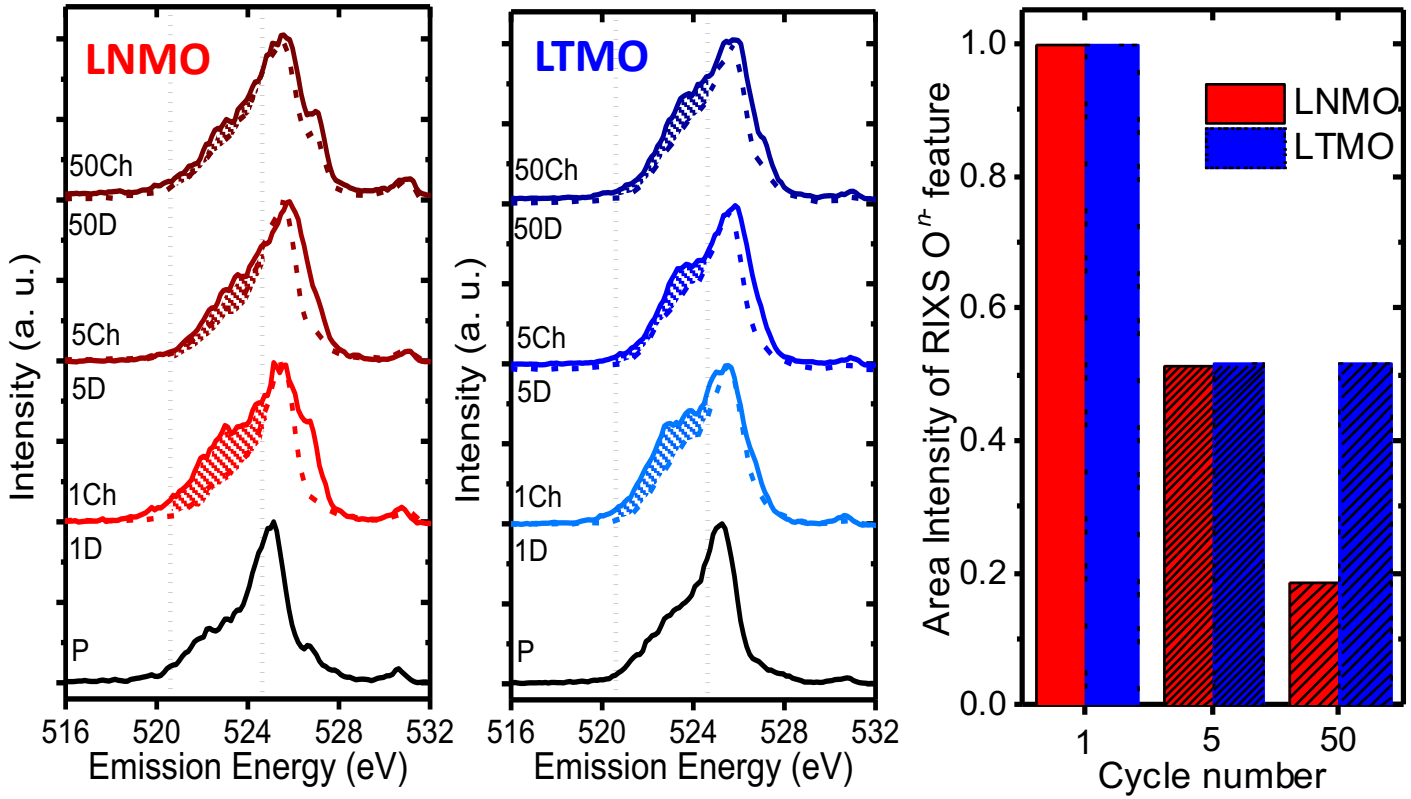




- Monitoring oxidized oxygen signal at ~ 531 eV reveals changes in redox activities of O with cycling
- Capacity decay correlated to the decrease in the intensity of oxidized oxygen

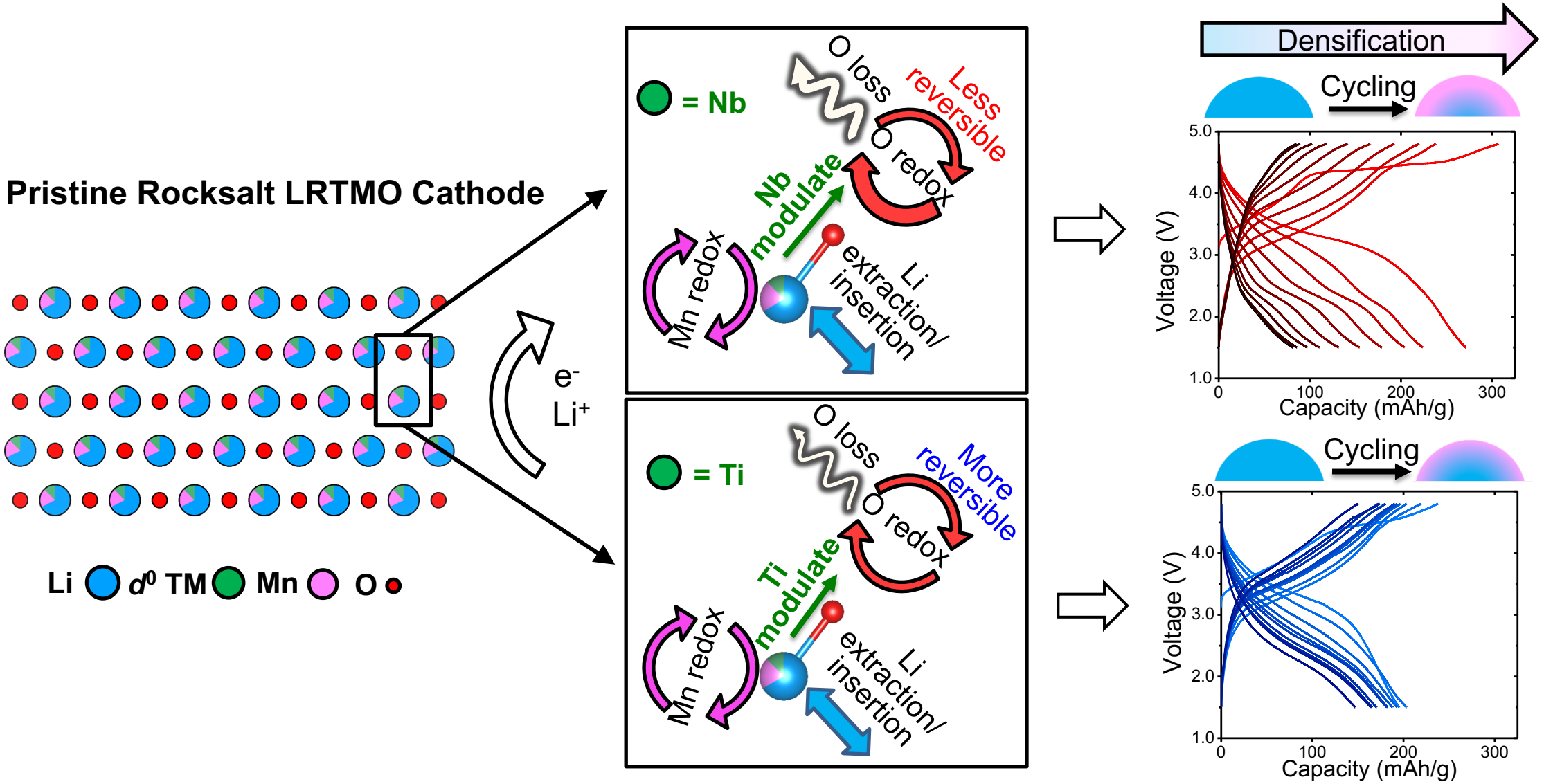
Strategy I – redox-inactive TM modulates stability of oxidized oxygen





- Evolution of oxidized oxygen involvement along with cycling quantified from RIXS cut emission spectra
- Ti better redox-inactive TM than Nb in stabilizing oxidized oxygen in the rocksalt LRTMO lattice

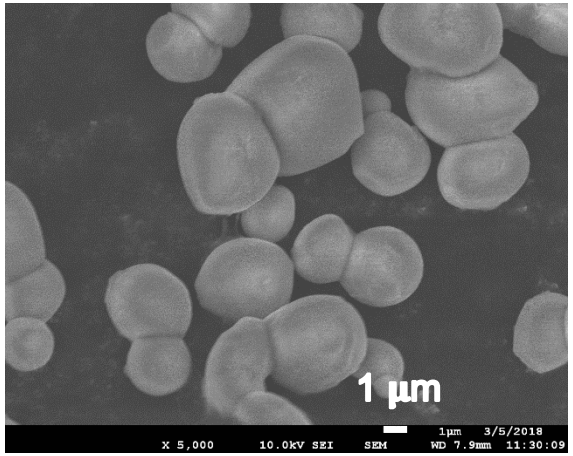
Strategy I – redox-inactive TM influences degradation mechanism



- Redox-inactive TM modulation – Ti improves reversibility of O redox while reducing O loss from the lattice

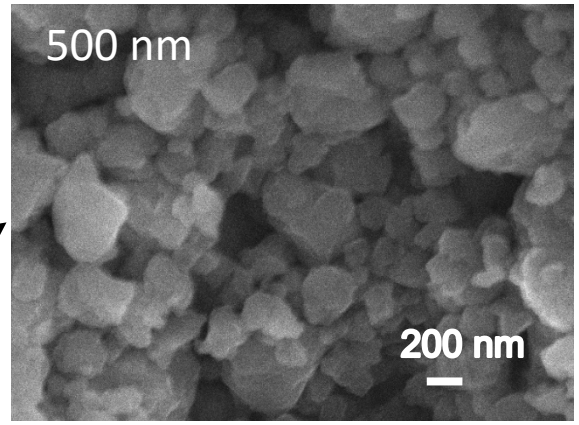
Mitigating Strategy II – Particle Engineering

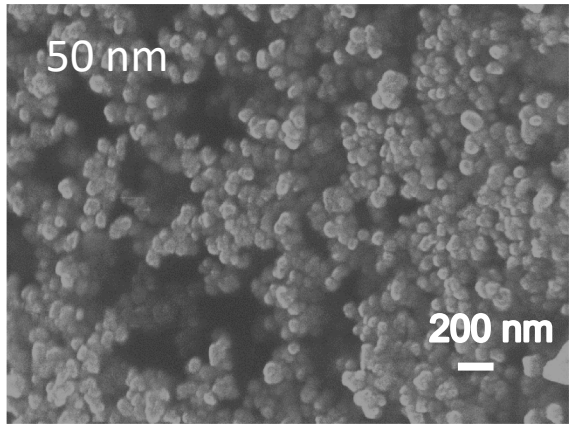
Synthesized LNMO crystals

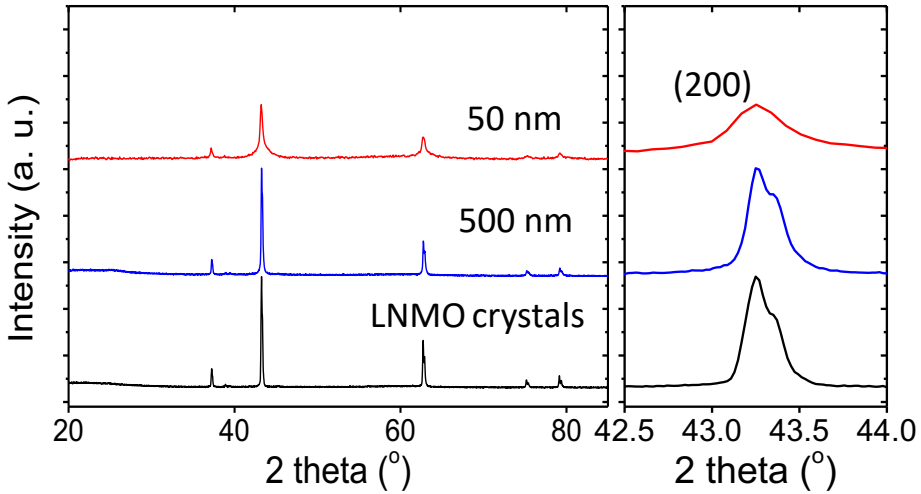


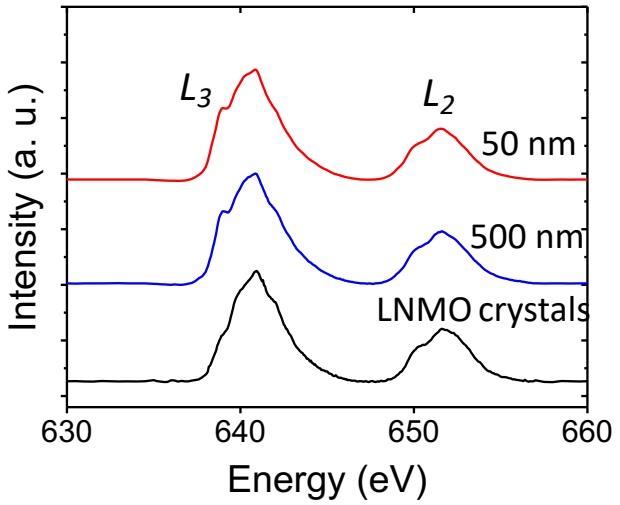
Low-speed ball milling

High-speed ball milling





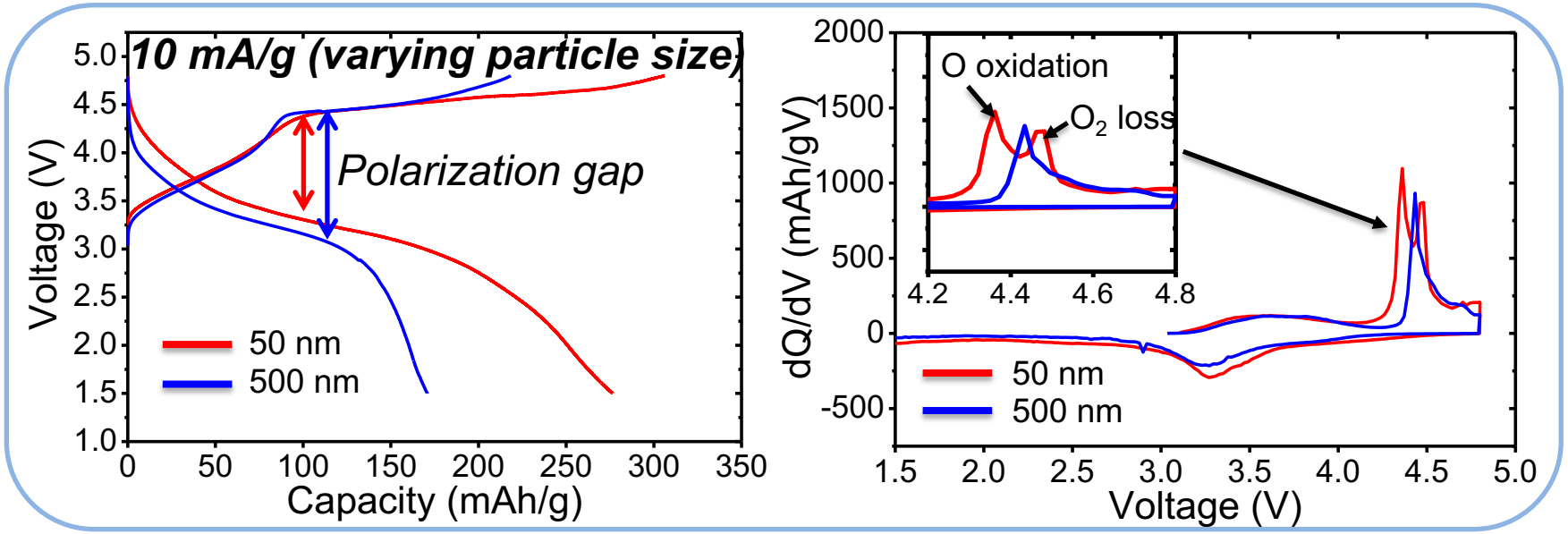


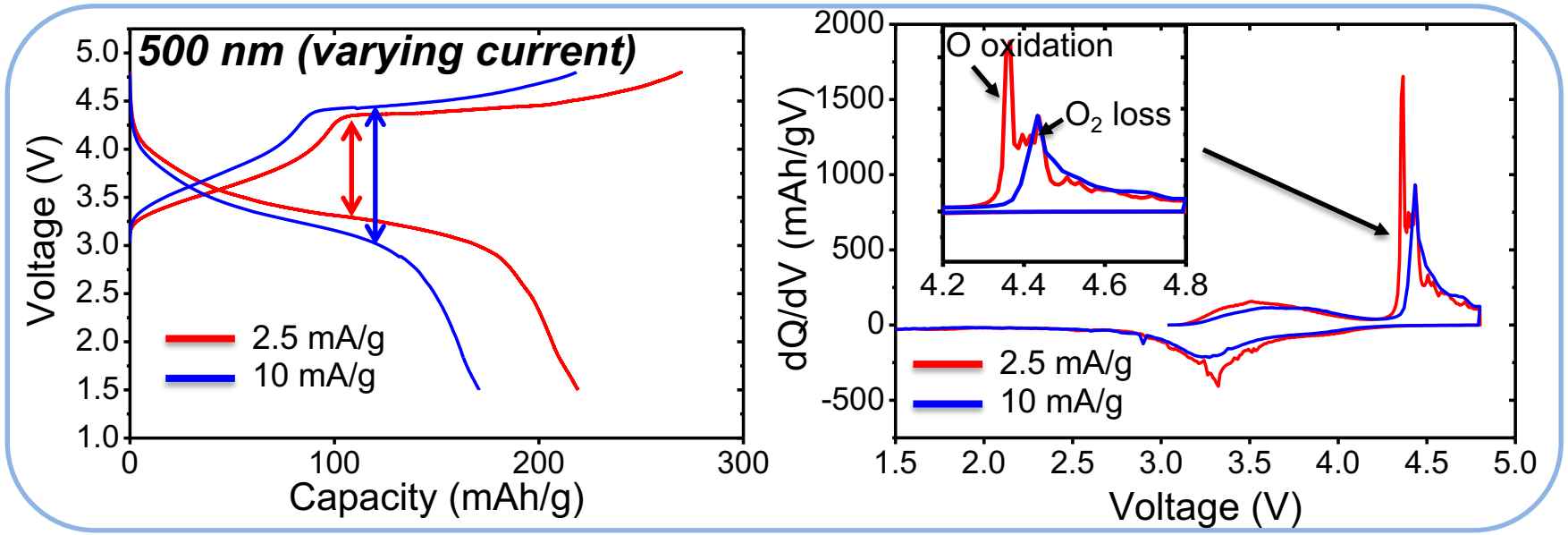


Mn L-edge TEY soft XAS (SSRL beamline 8-2)

- Two LNMO samples prepared with the same crystalline orientation but different particle size of 50 nm and 500 nm.
- Smaller particles show peak broadening on XRD but crystal structure and Mn oxidation state maintained.

Strategy II – effect of particle size on O redox

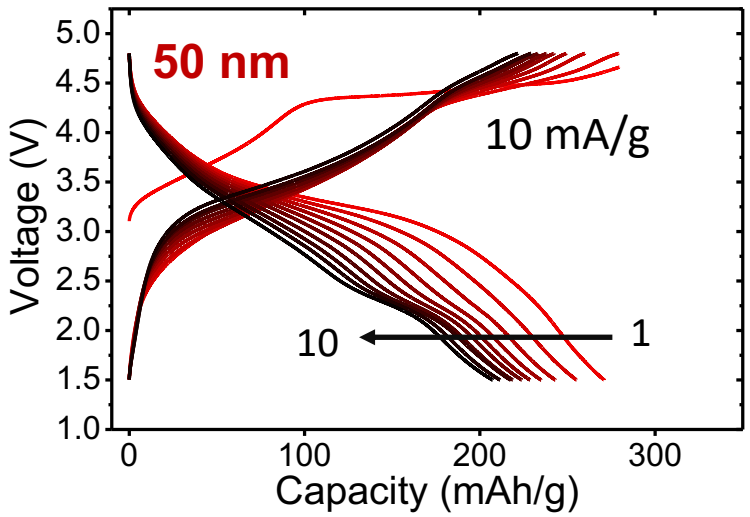


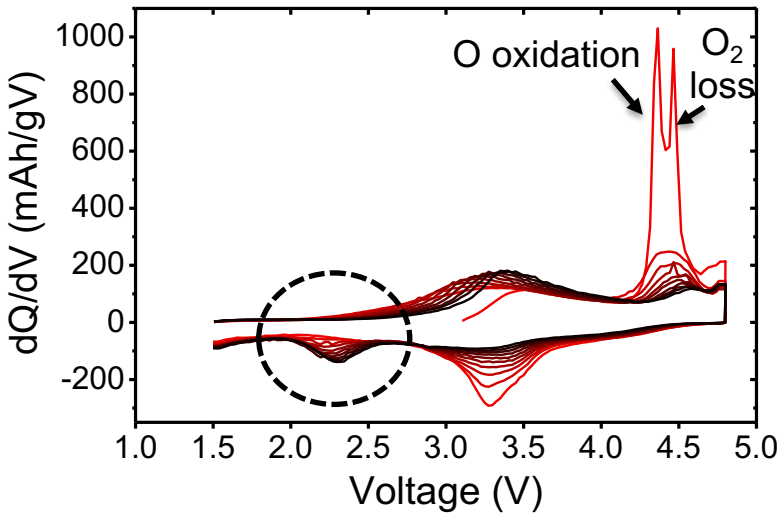


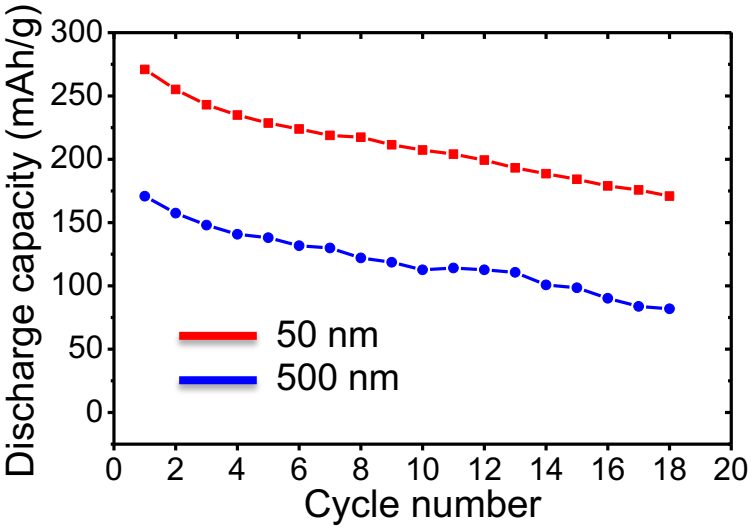
Reducing particle size leads to:

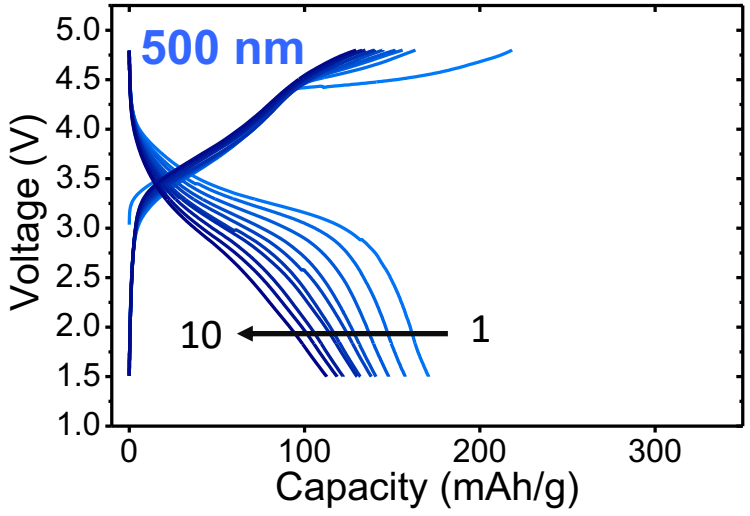
- Reduced polarization gap between charge and discharge
- Decreased O oxidation potential and the separation from O_2 release peak
- No significant changes in Mn redox
- Much of these observation can be achieved when a slower rate is used, indicating a kinetic effect

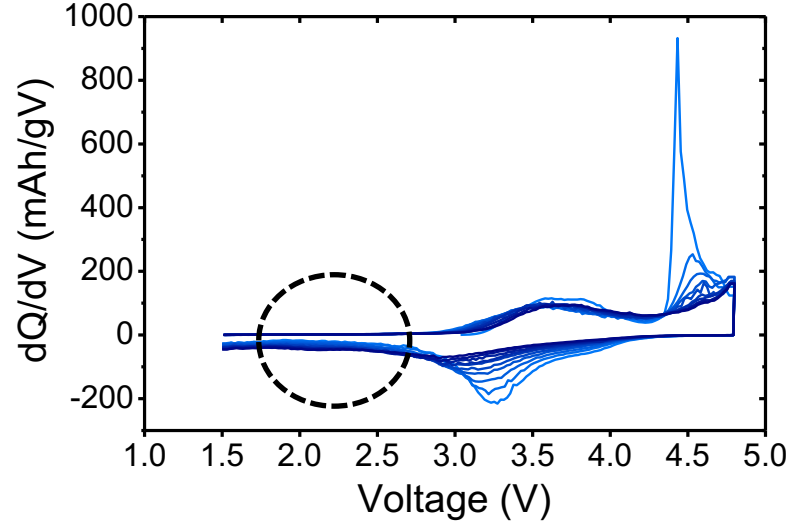
Strategy II – effect of particle size on cycling stability

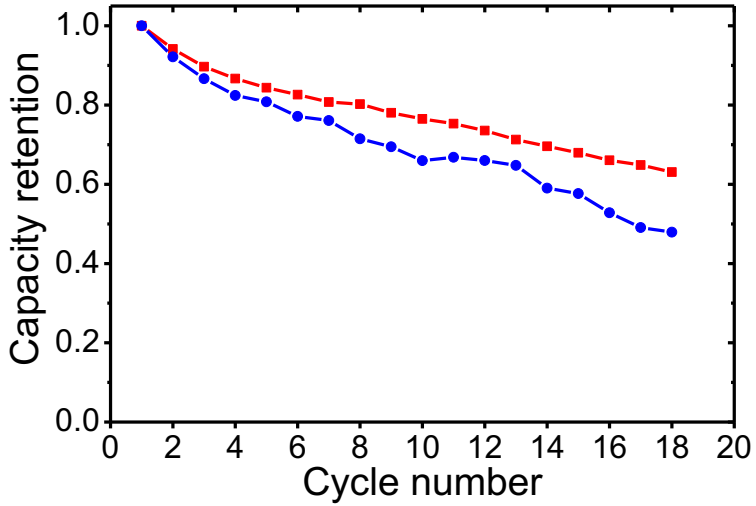








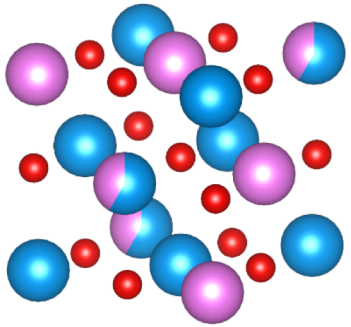


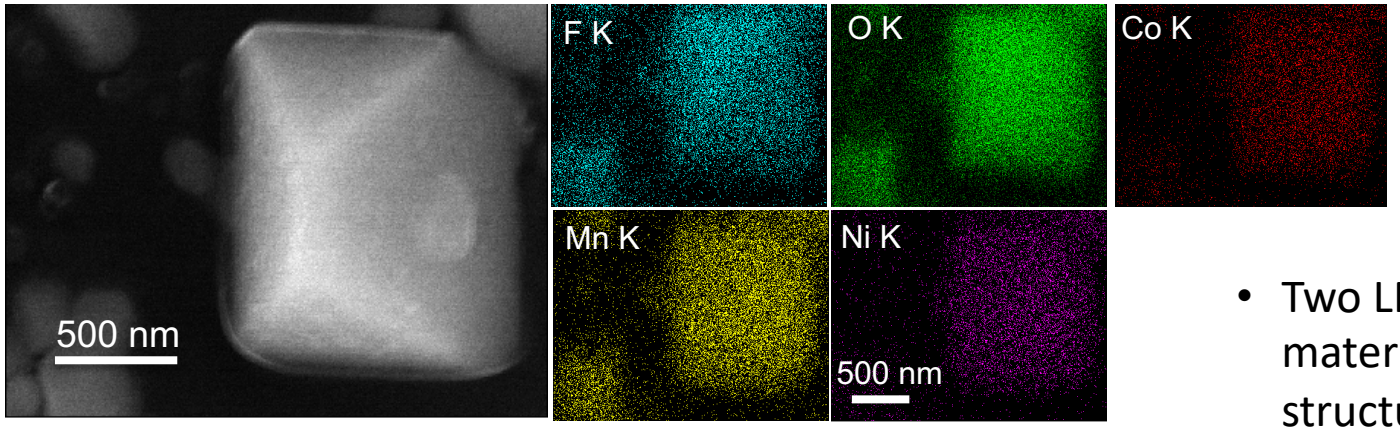


- Reducing particle size improves kinetics but also increases O loss due to enhanced surface area.
- Overall improved capacity and cycling stability in smaller parties suggest particle downsizing benefits more on O redox.

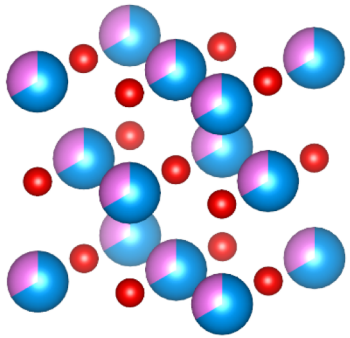
Mitigating Strategy III – Particle Surface Modification

Layered LMR-NMC
($Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$)

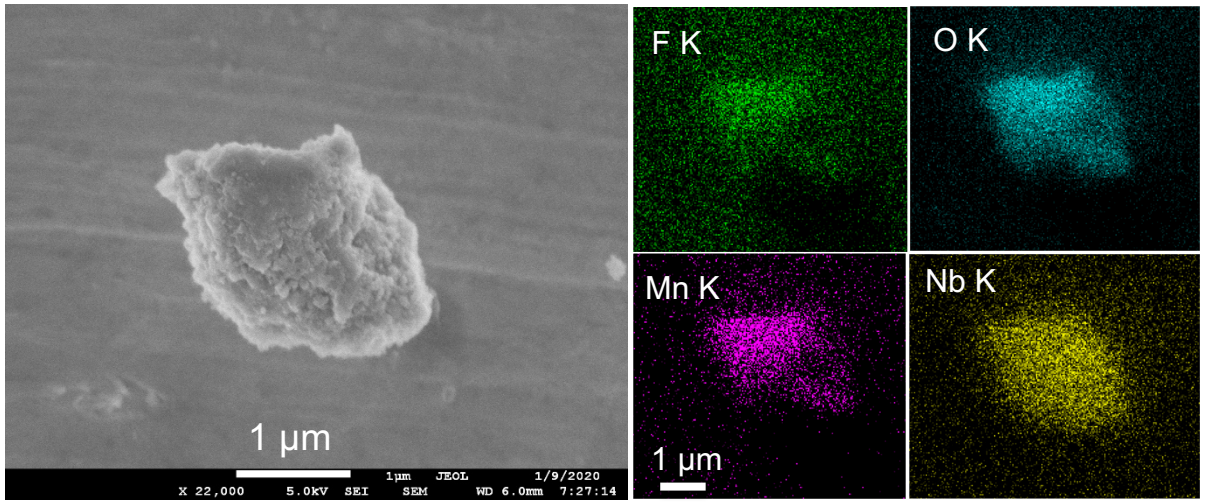




Rocksalt LNMO

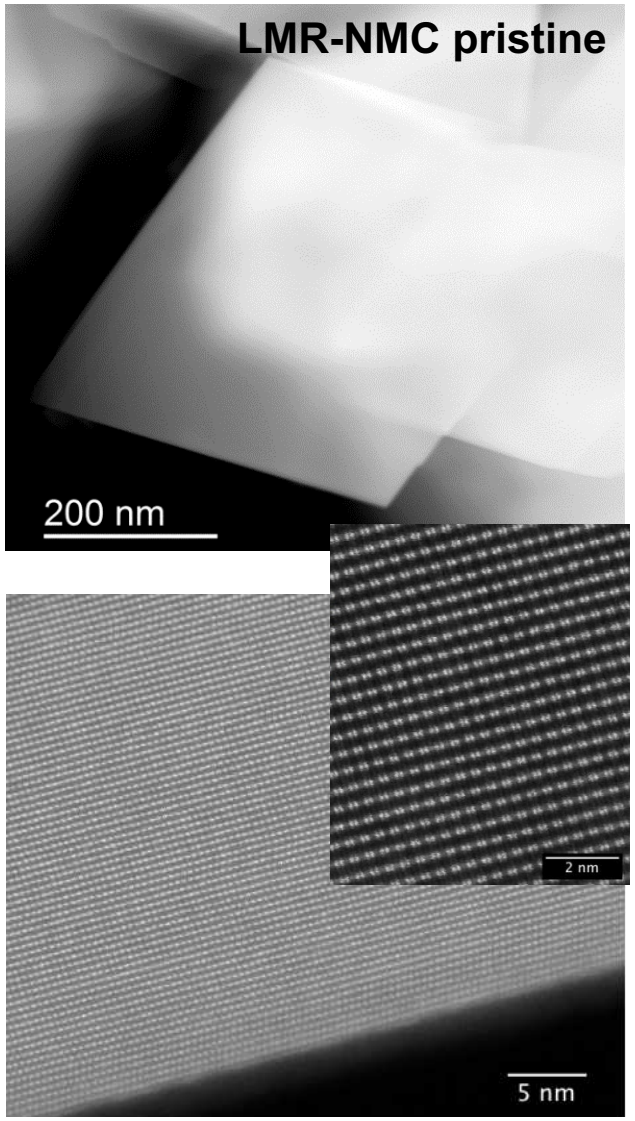


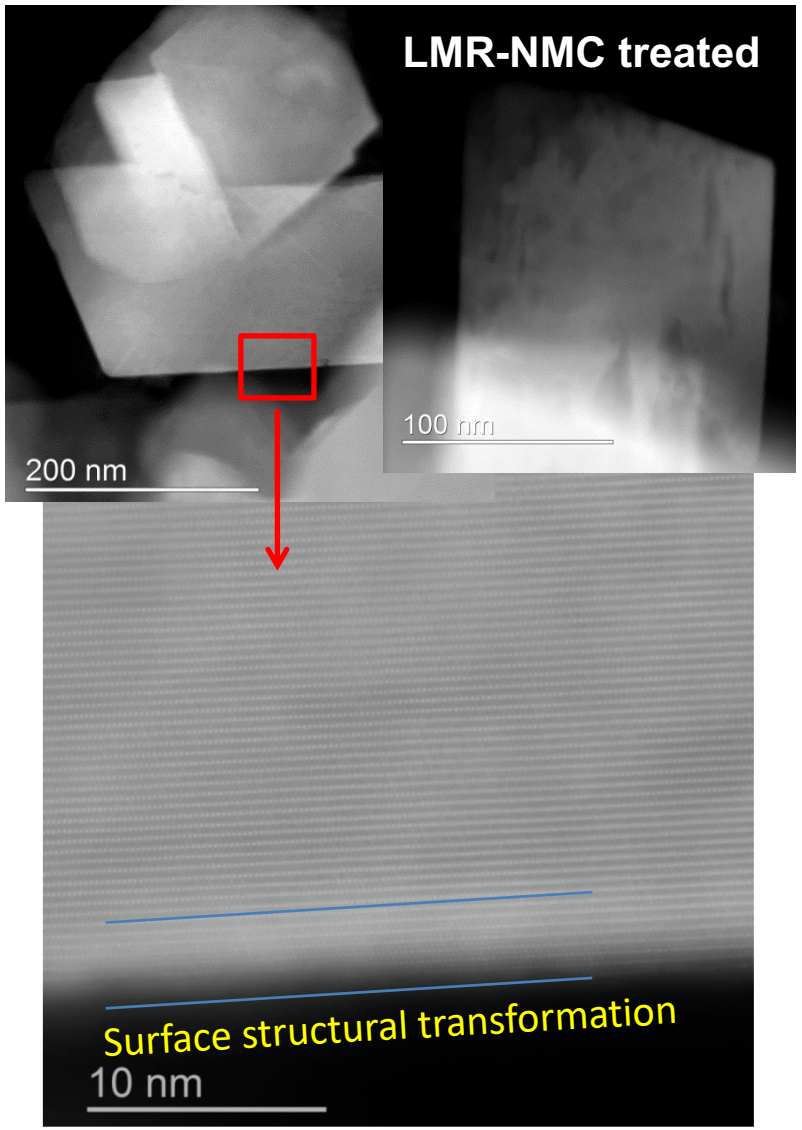
Li TM O



- Two LRTMO cathode materials, a layer-structured LMR-NMC and a rocksalt-structured LNMO were each surface treated with 5 wt.% NH_4F at 300 ^oC in air.
- Even coverage of F on particle surface detected by EDX, suggesting uniform treatment at particle level.

Strategy III – effect of surface modification on crystal structure

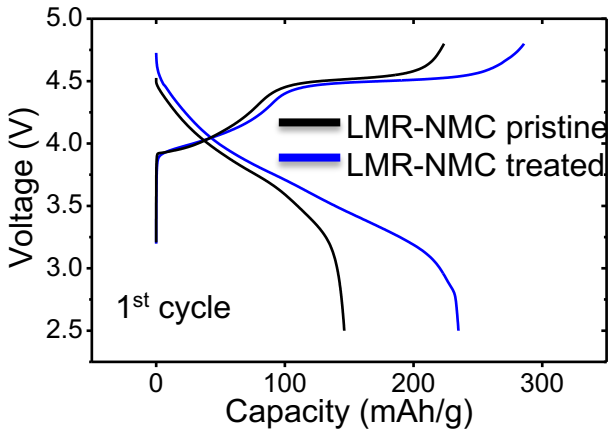


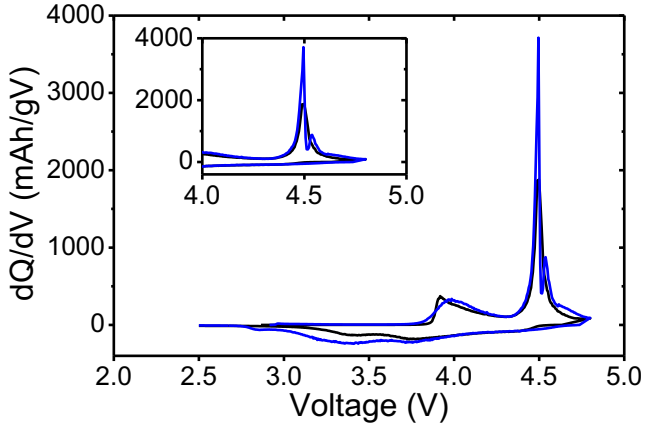


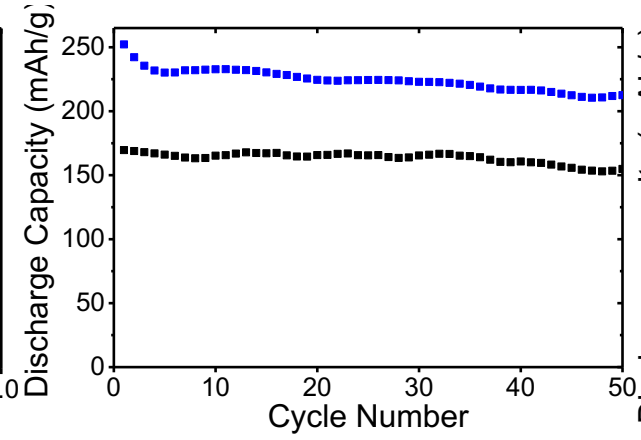
STEM imaging
(with C. Wang, PNNL)

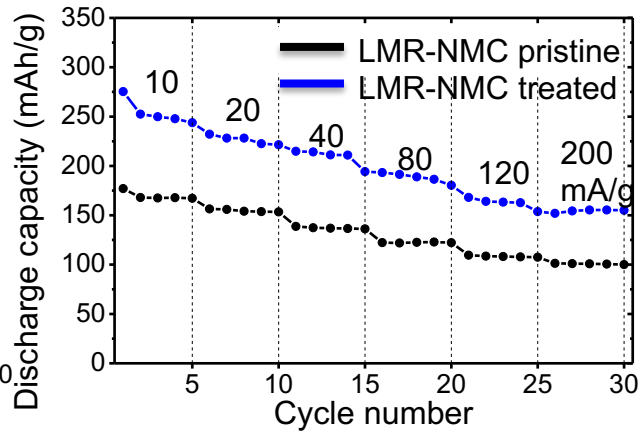
- Pristine LMR-NMC sample has octahedron shape with a smooth surface and layered crystal structure.
- Surface treatment maintains particle shape but leads to roughing of the oxide surface.
- Surface treatment transforms the crystal structure of the top few nm planes aligned with the direction of TM stacking layer into a denser atomic arrangement.

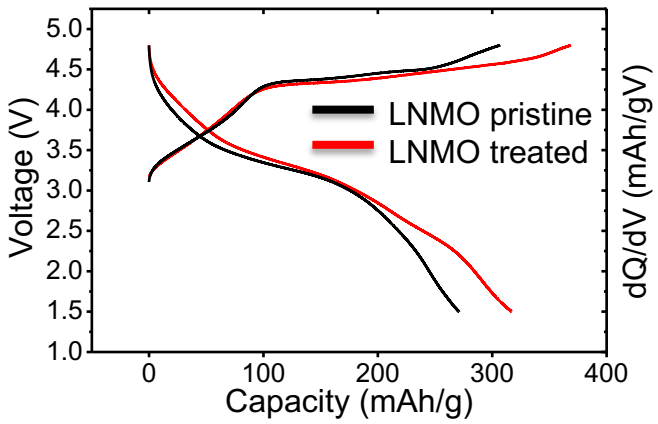
Strategy III – effect of surface modification on O redox and kinetics

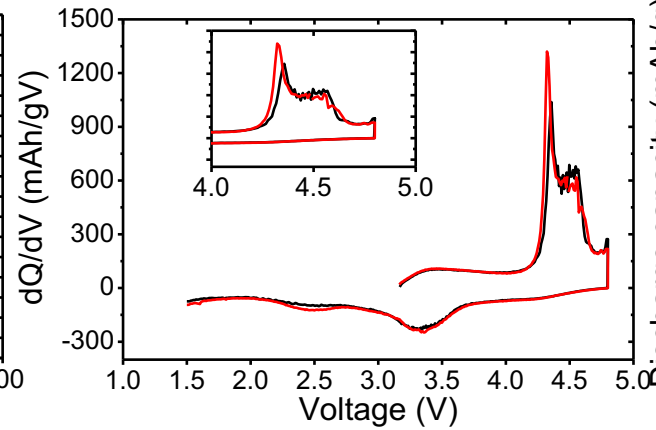


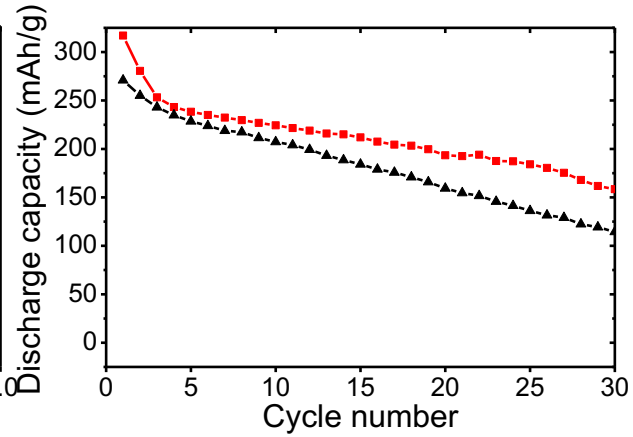


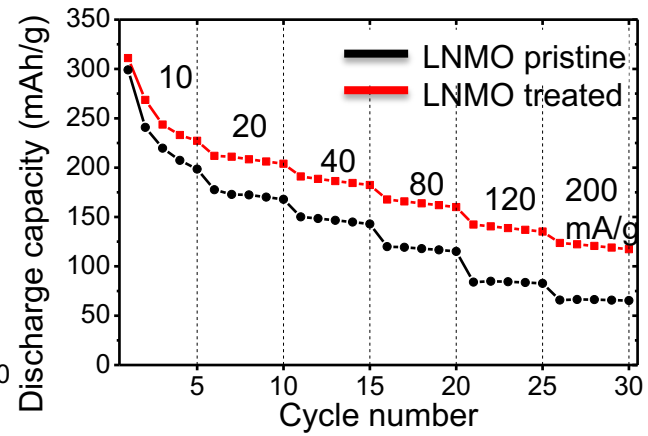






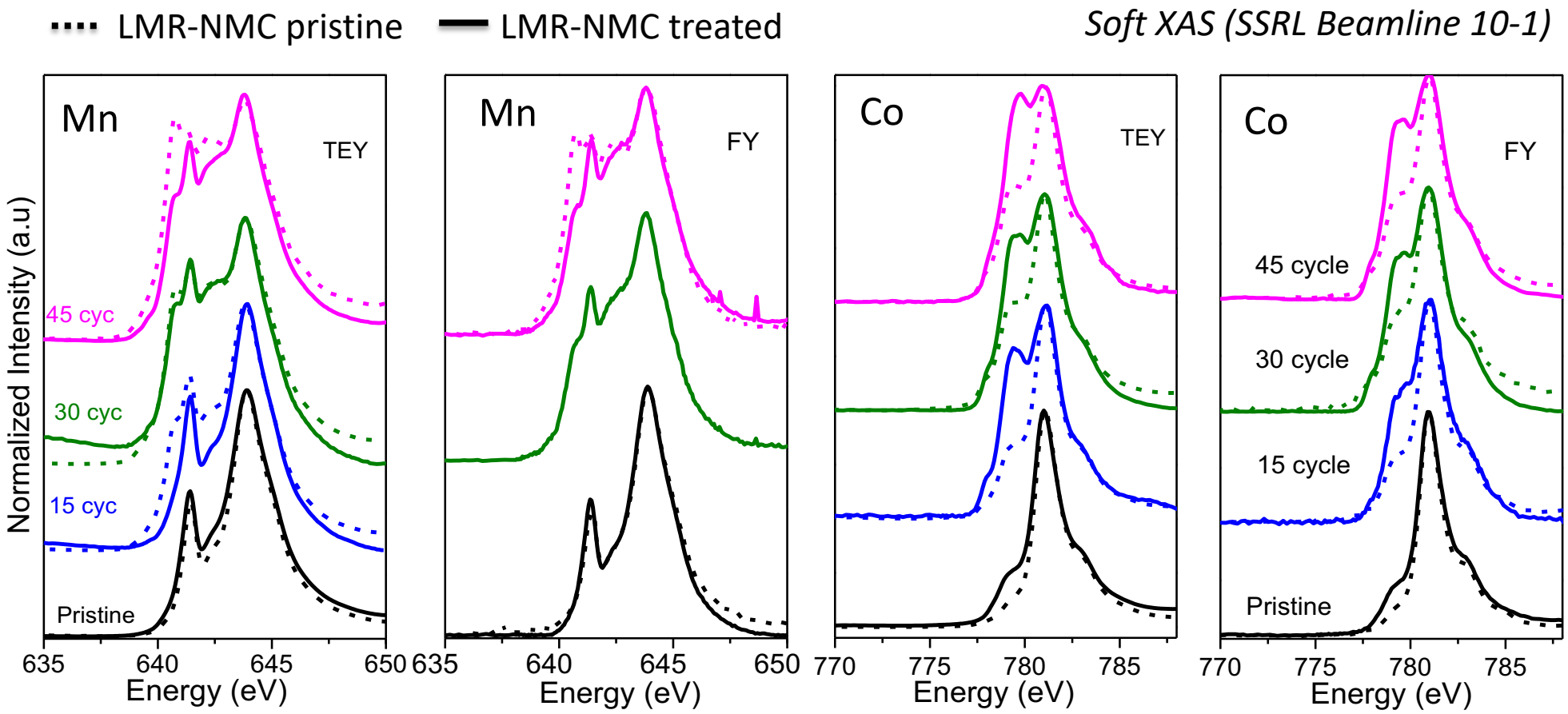






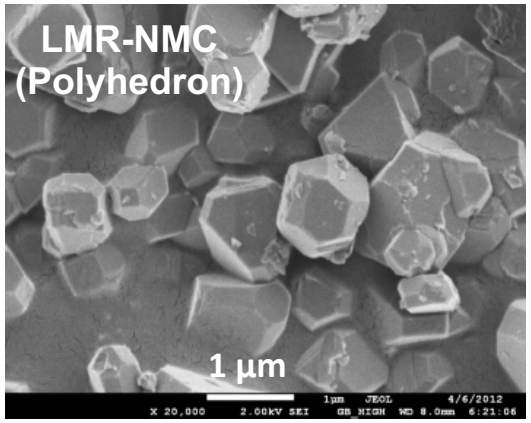
- Surface modification increases capacity and improves O redox process and kinetics in both layered and rocksalt structured LRTMO cathodes
- The improvement likely a result of surface roughing that enhances surface area, which increases utilization of the active materials and kinetics

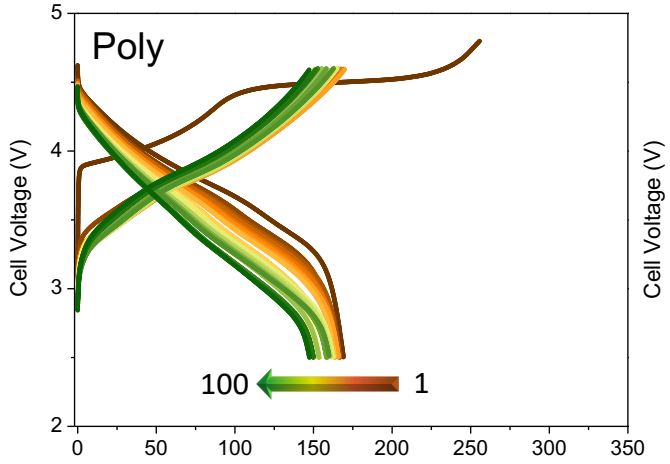
Strategy III – effect of surface modification on chemical changes

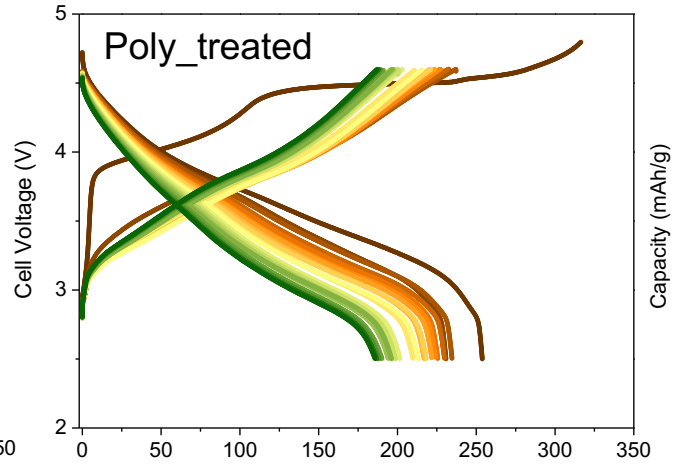


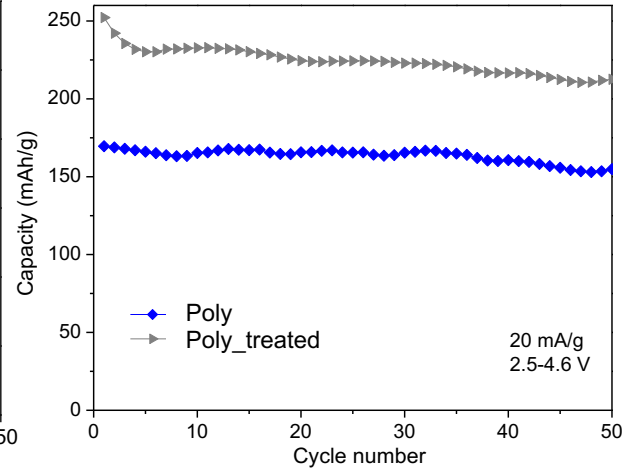
- Surface modification decreases Mn reduction but increases Co reduction after cycling – a decoupling effect.
- Comparison of TEY (probing depth of ~5nm from surface) and FY (probing depth of ~50 nm) spectra reveals the effect most significant on the surface.

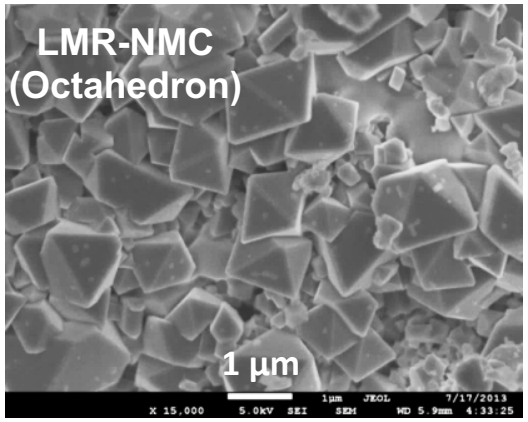
Strategy III – effect of surface modification morphology dependent

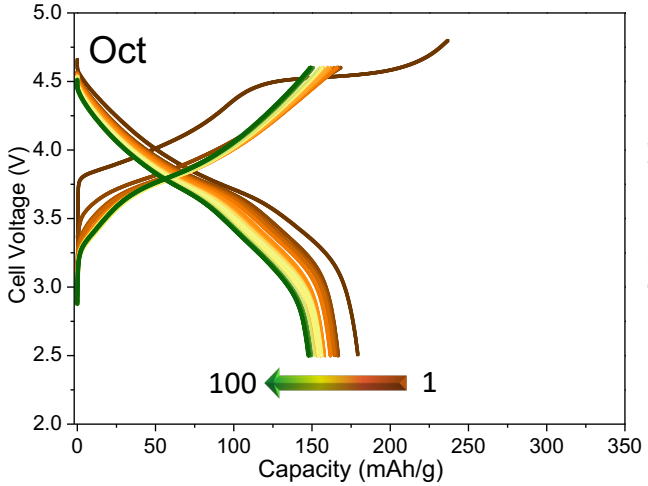


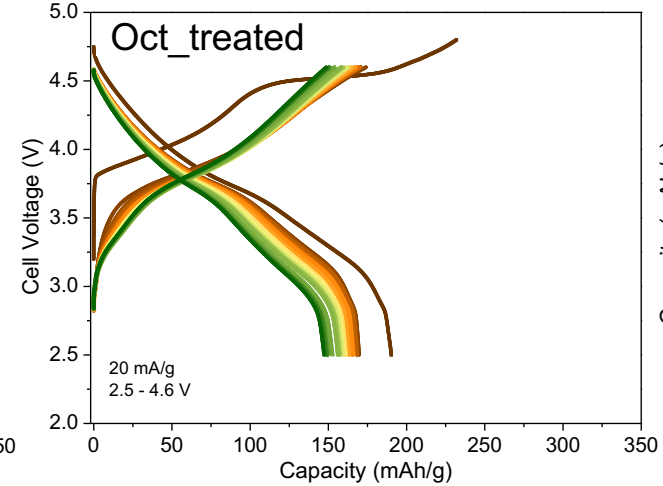


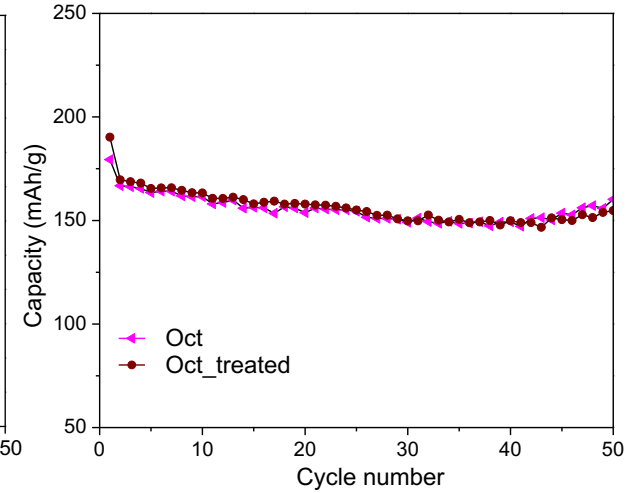












- Facet-dependent behavior of surface treatment - modification effect not significant on the sample with octahedron-shaped particles.
- Surface treatment studies need to take consideration of pristine sample properties.

Responses to Previous Year Reviewers' Comments

A total of five reviewers evaluated the project. Overall, the reviewers' comments were very positive. They noted that "the approach was well developed and the work done was of high quality", "excellent progress has been accomplished" and "the work clearly shows a great collaborative effort". Specific comments and suggestions are addressed below:

Recommendation/Comment: The reviewer wanted to know whether the carbon dioxide (CO2) release occurs at a potential below 4V and how the CO2 is released during the second cycle.
Response/Action: CO_2 release begins around 3.8 V during the charge. In the second cycle, CO_2 release was also detected but in a much smaller quantity.

Recommendation/Comment: The reviewer said it would be interesting to have seen how anion dopants help further stabilize the O2, as well as doping on the Mn transition metal and increasing the total Li concentration.
Response/Action: The work relating to anion doping as well as doping of redox-active Mn is being performed in a separate project in the DRX (cation-disordered rocksalt as cathode active materials) program.

Recommendation/Comment: On the DEMS, it looks like at high voltages on discharge, there is a plateau whereas in normal systems, it is not shown. The reviewer asked why this is manifesting and how it will change the results when not present. The reviewer indicated the team claims that Ti4+ is better than Nb5+ in suppressing molecular O2 loss. However, with the weird voltage profile, these results might be muddled, and more work is needed to identify this.
Response/Action: We added a rest step between the charge and discharge in the DEMS measurements and that is the reason for the plateau shown at high voltages on discharge. We do not believe this changes our conclusion as it is also supported by the electrochemical evaluation, where the incremental voltage profiles clearly show significant difference in O redox activities when Ti4+ and Nb5+ were used.

Recommendation/Comment: The role of the university investigator is not clear.
Response/Action: The DEMS work was a close collaboration with our UC Berkeley collaborator, Prof. Bryan McCloskey.

Responses to Previous Year Reviewers' Comments (Cont'd)

Recommendation/Comment: The reviewer encouraged the PI to develop research questions that take full advantage of the use of single crystalline materials (e.g., surface of different facets).
Response/Action: We thank the reviewer for the excellent suggestion. We have included work on surface treatment this year where single crystalline samples with different surface facets were used to investigate surface modification effect. The results clearly demonstrate the unique advantage of using our well-controlled model samples.

Recommendation/Comment: The reviewer asked if there is a pathway moving forward to increasing the electrode loading.
Response/Action: As we only make high-quality samples in small batch size in the laboratory setting, it is difficult for us to make thick electrodes mimicking those used in the commercial batteries. However, as our study aims to evaluate the fundamental changes occurring on the cathode materials during battery operation, we believe the findings relate to material's intrinsic behavior and they still apply in thicker electrodes used in commercial settings.

Collaborations

- Prof. Gerd Ceder and Kristin Persson (UC Berkeley) – modeling
- Drs. Marca Doeff (LBNL), Dennis Nordlund and Yijin Liu (SSRL), and APS – synchrotron *in situ* and *ex situ* XRD, XAS and FF-TXM-XANES studies
- Drs. Wanli Yang and Nobumichi Tamura (ALS) – synchrotron XAS/RIXS and micro-XRD studies
- Prof Bryan McCloskey (UC Berkeley) – DEMS
- Drs. Jagjit Nanda, Ashfia Huq (ORNL) and Jack Chen (Chinese Academy of Sciences, CAS and ANSTO) – neutron diffraction and PDF studies
- Dr. Chongmin Wang (PNNL) – STEM/EELS

ALS ADVANCED LIGHT SOURCE

SSRL

Pacific Northwest NATIONAL LABORATORY

Berkeley UNIVERSITY OF CALIFORNIA

Australian Government ANSTO

BERKELEY LAB Lawrence Berkeley National Laboratory

Advanced Photon Source ARGONNE NATIONAL LABORATORY

CHINESE ACADEMY OF SCIENCES

OAK RIDGE NATIONAL LABORATORY MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Remaining Challenges and Barriers

- Use of Li metal anode coupled with a solid-state electrolyte (SSE) offers most promising pathway to high-energy and safe batteries but significant developmental barriers exist
- Fundamental knowledge of performance- and stability-limiting properties and processes in solid-state electrolytes limited
- Knowledge on reactivities between the SSE and Li metal anode and insights on the dynamic evolution of the electrolyte/anode interface limited
- Knowledge on reactivities between the SSE and high-energy cathode and insights on the dynamic evolution of the electrolyte/cathode interface limited
- Need of better functional materials (particularly SSEs) and interfaces to enable high-energy Li metal based batteries

Proposed Future Work

- Develop and synthesize model samples and model interfaces suitable for studying rate- and stability-limiting properties and processes in Li metal based batteries
- Advanced diagnostic studies of SSE model samples at both particle-level and bulk-sample level
- Obtain understanding on SSE grain and grain boundary chemistry, properties, and their effect on ion conduction and dendrite formation at the Li metal anode interface
- Investigate the reactivities between model SSE and electrode interfaces and gain insights on the dynamic evolution of the SSE/electrode interfaces

"Any proposed future work is subject to changes based on funding levels."

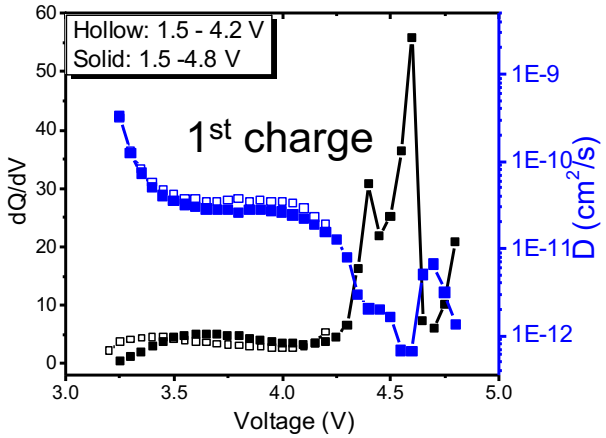
Summary

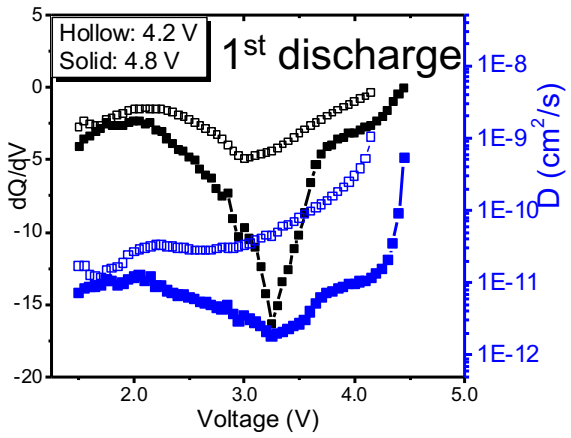
- High-quality LRTMO cathode model samples were synthesized for diagnostic studies
- Degradation mechanism in rocksalt-structured LRTMO cathodes elucidated
- Strategies to improve O redox and its better utilization for developing high-energy cathode materials evaluated

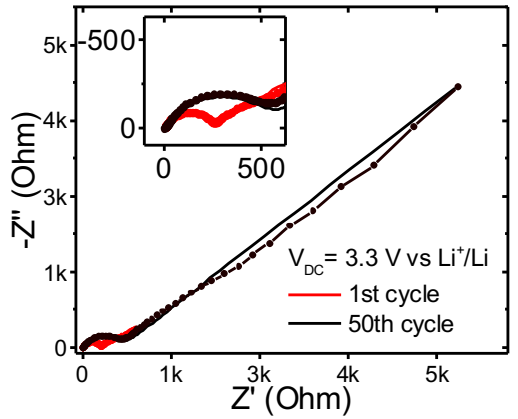
1. Chemistry engineering to increase stability of O redox
   - Redox-inactive TMs found to modulate oxygen redox activities
   - Ti better stabilizer than Nb
2. Particle engineering to improve utilization of O redox
   - Reducing particle size improves cathode kinetics but also increases O loss because of larger surface area
   - Reducing particle size improves overall performance as benefits outweigh drawback
3. Post-synthesis surface treatment to improve LRTMO cathode performance
   - Surface treatment improves capacity and kinetics but effect largely depends on particle morphology.

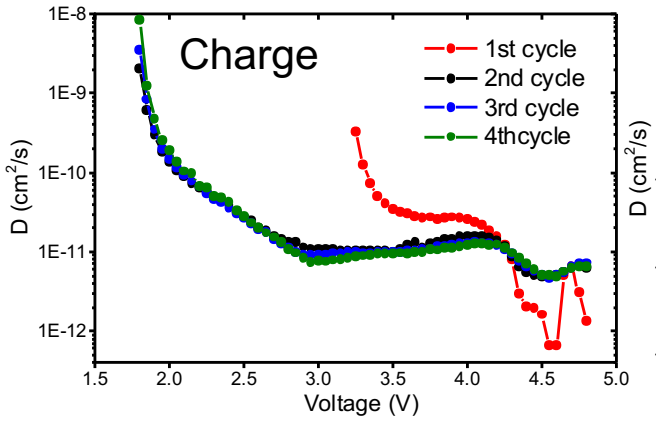
Technical Back-Up Slides

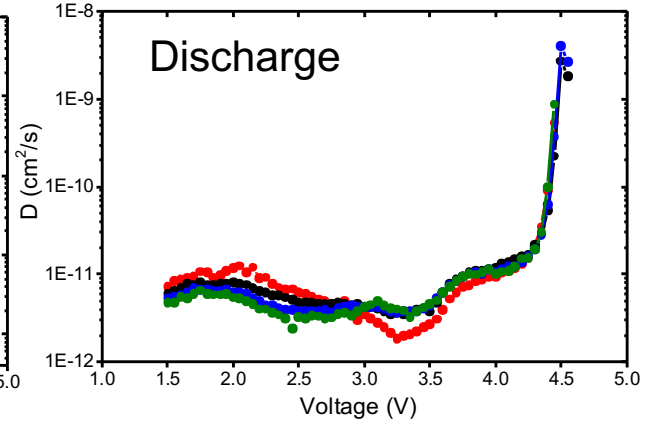
LRTMO rate capability correlated to extent of O redox

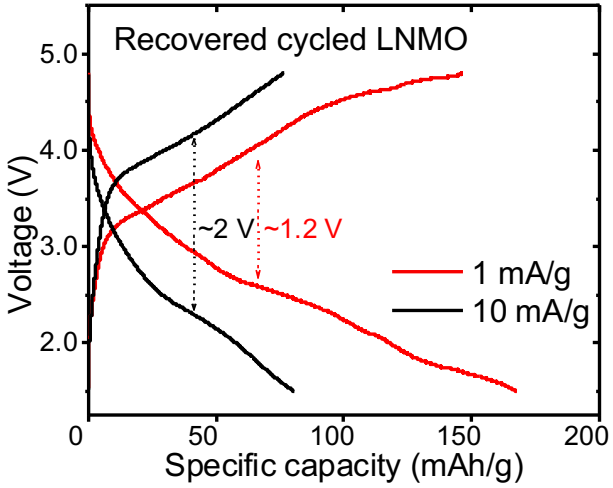






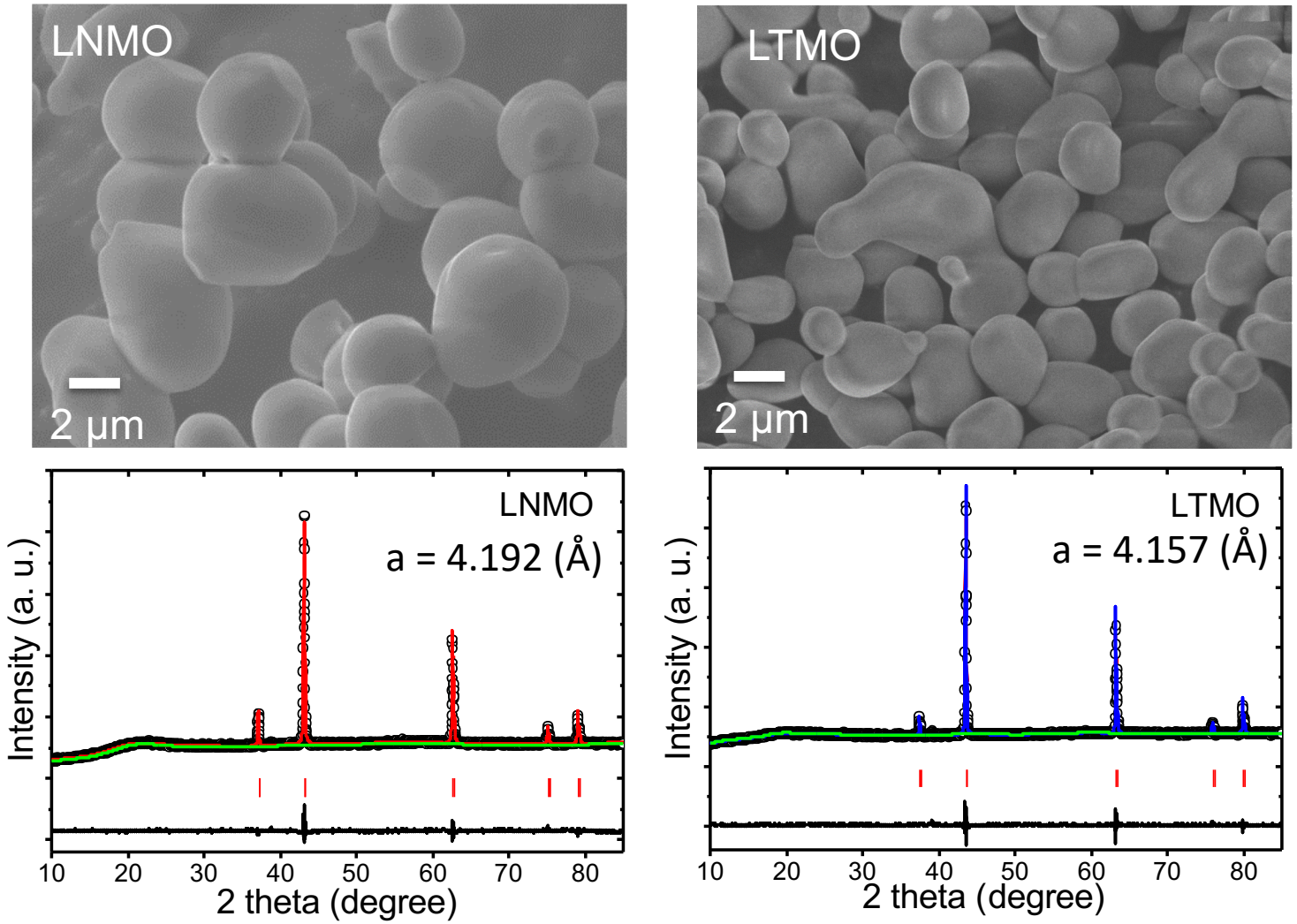






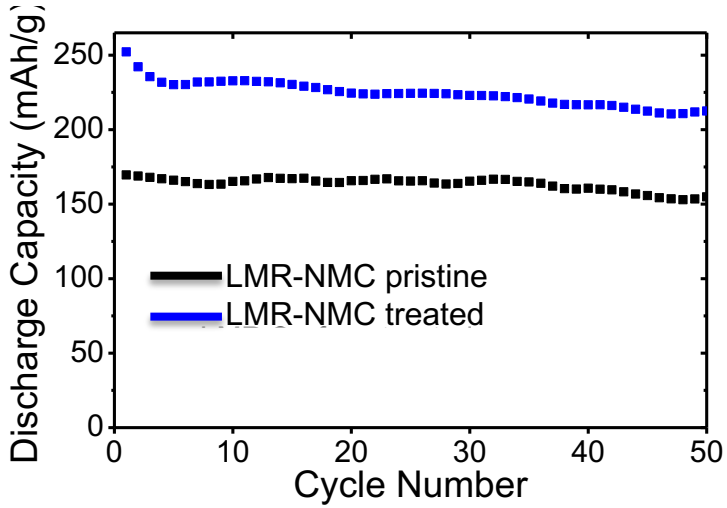
- Oxygen redox has poor kinetics and repeated cycling involving oxygen reduces TM redox kinetics as well.
- Significant capacity recovery of cycled cathode at slower rate – kinetic barrier major source of performance degradation.

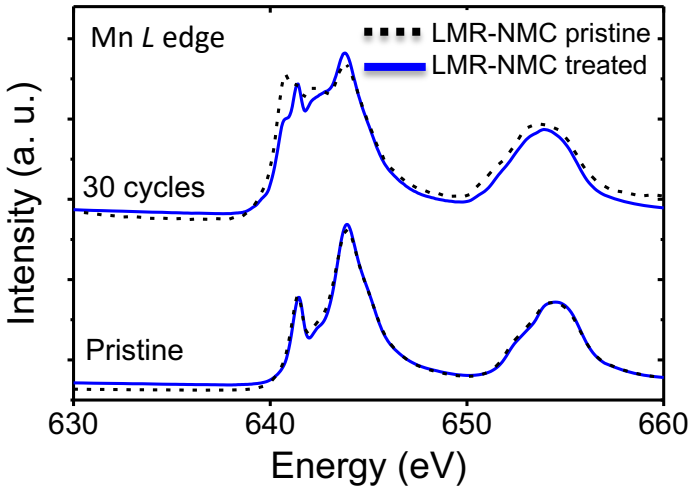
Characterization of LRTMO with varying redox-inactive TM

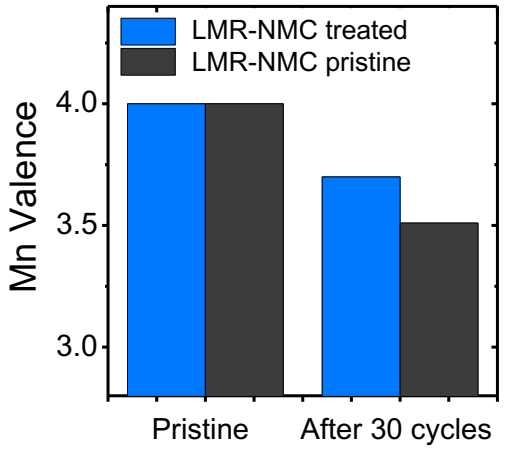


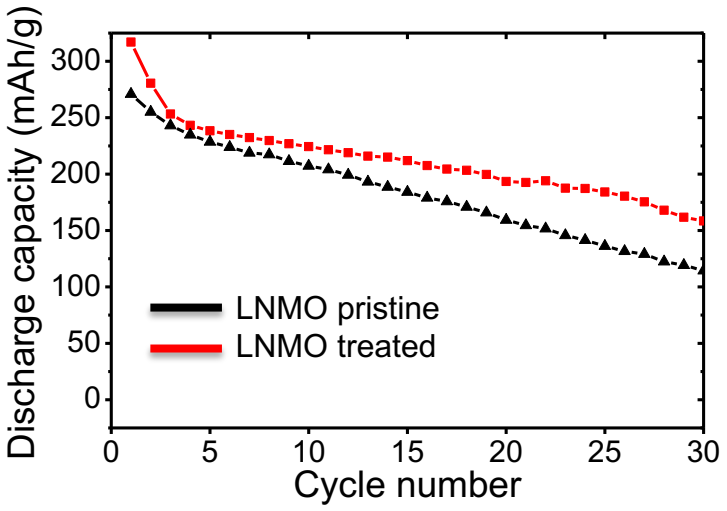
- Well-formed, phase-pure and rocksalt-structured LNMO and LTMO model samples were obtained for diagnostic studies

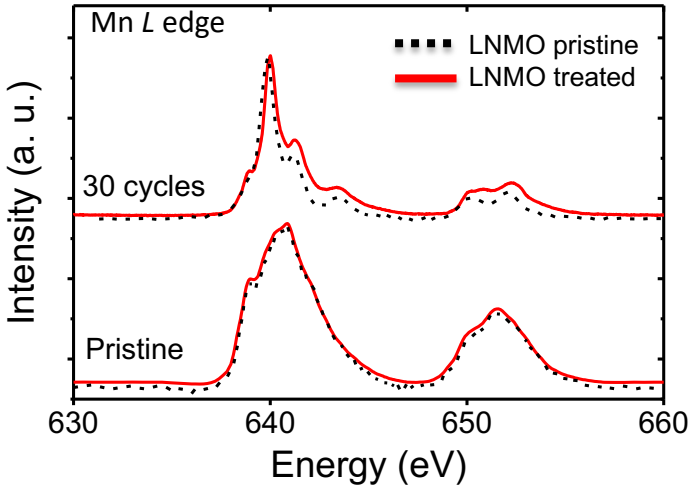
Effect of surface modification on surface chemical stability

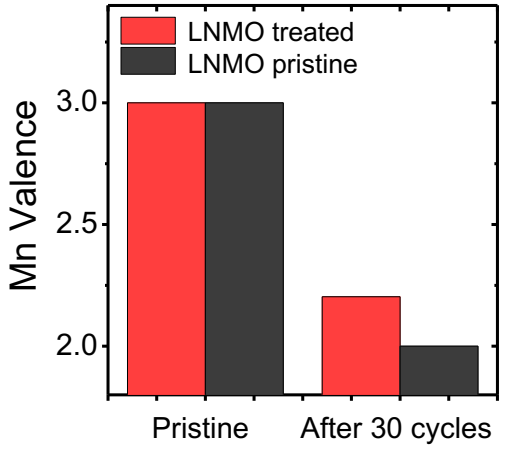






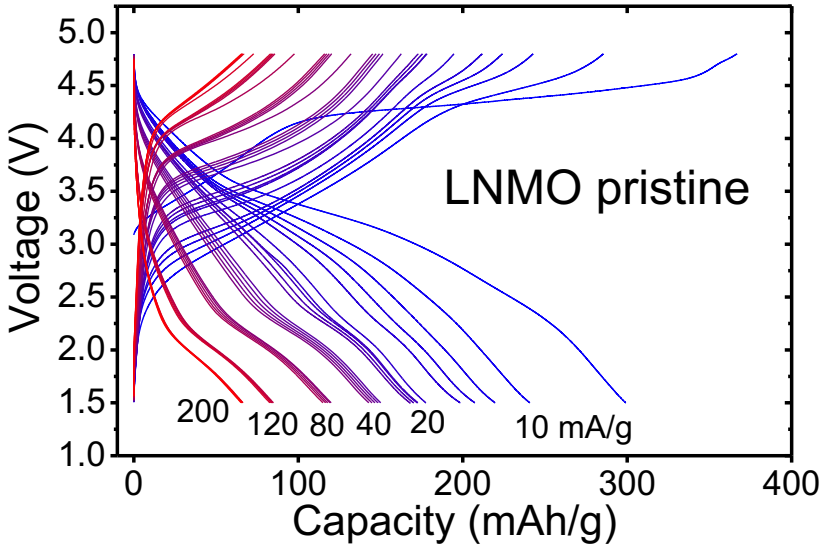


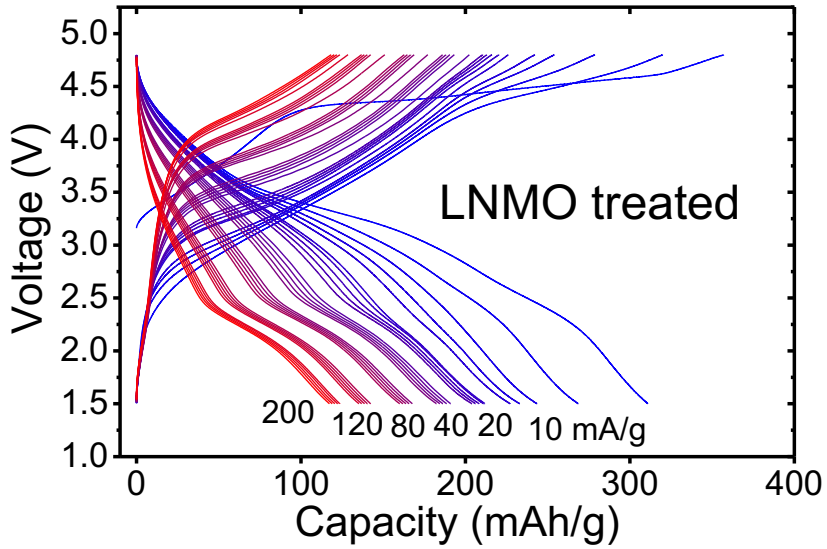


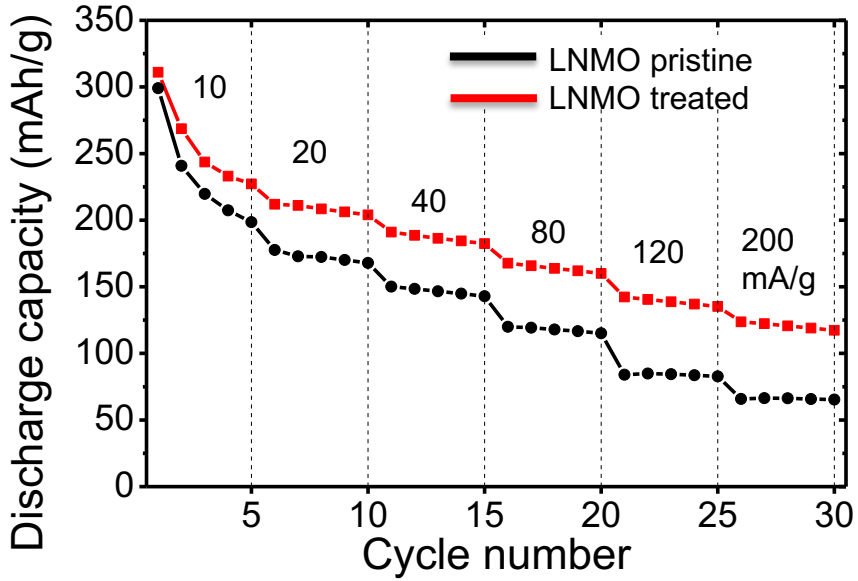


- Surface modification improves cycling stability and chemical stability of Mn on the surface

Effect of surface modification on polarization







- Increasing charge/discharge rate increases polarization – kinetic limitation in LNMO
- Surface modification reduces polarization and increases capacity at all rates tested